

Multilayered Hyperbolic Metamaterial using 2D MoS₂ as Constituent

Metamaterial Hiperbólico Multicapa Utilizando MoS₂ Bidimensional como Constituyente

Presented by:

Ramón Camilo Domínguez Ordóñez

Bachelor Thesis

Supervision

Jose Luis Ocaña Pujol

Dr. Henning Galinski

Project Director

Eidgenössische Technische Hochschule Zürich (ETH Zürich)

(Chair: Prof. Dr. Ralph Spolenak)

Prof. Dr. German A. Perez

Project Co-Director

Universidad del Valle

December 12, 2023

Abstract

This research delves into the emerging potential of molybdenum disulfide (MoS_2), a transition metal chalcogenide, which has shown promising applications in optoelectronic devices since the global growth of Graphene, owing to its unique tunability of the functional properties with thickness. In the face of conventional fabrication techniques like exfoliation and CVD struggling with scalability and coverage issues, this work introduces a novel two-step bottom-up magnetron sputtering deposition process for synthesizing MoS_2 films. This method stands out for its versatility in depositing both amorphous and crystalline MoS_2 and its industrial manufacturing scalability, spanning from nanoscale to bulk thicknesses in various architectures. Utilizing a custom-designed *Mathematica* code based on the Transfer Matrix Approach (*TMA*) and Fresnel equations, we simulated the optical properties and a complete color palette of our produced MoS_2 , achieving remarkable alignment with experimental observations. By exploiting the freedom in substrate choice, control over thickness, and the annealing process, we established a correlation between the optical and electrical properties of the material. Furthermore, we demonstrated the method's efficacy in fabricating a MoS_2 -based hyperbolic metamaterial by initially simulating the multilayer structure and phase diagram in a *Mathematica* code based on Effective Medium Theory (*EMT*) to determine the quantity of our composite to obtain the interesting hyperbolic dispersion relationship, highlighting its potential in advanced optoelectronic applications. Collectively, our study not only underscores the multifaceted advantages of the proposed deposition technique and the same material trends reported in the literature for MoS_2 including the increase of the resistivity with both crystallinity and film thickness, but also paves the way for innovative MoS_2 -based device developments.

Key words: Transition Metal Dichalcogenides (TMDCs), Molybdenum Disulfide (MoS_2), Magnetron Sputtering, Heat Treatment, Film Thickness Control, Size Effects, Transfer Matrix Approach (*TMA*), Effective Medium Theory (*EMT*), Hyperbolic Metamaterial, Optical Properties, Electrical Properties, Industrial Scalability, Optoelectronic Devices, Raman Spectroscopy, Rutherford Backscattering, Ellipsometry, Reflectance, X-ray Diffraction, Four-Point Probe Method

Resumen

Esta investigación profundiza en el potencial emergente del Disulfuro de Molibdeno (MoS_2), un calcogenuro de metal de transición. Desde el auge global del Grafeno, el MoS_2 ha demostrado aplicaciones prometedoras en dispositivos optoelectrónicos debido a su capacidad única de modificar sus propiedades funcionales según su grosor. Frente a técnicas de fabricación tradicionales, como la exfoliación y el CVD, que enfrentan retos de escalabilidad y cobertura, este trabajo propone un innovador proceso de deposición por pulverización catódica magnetrónica en dos etapas, desde abajo hacia arriba, para sintetizar películas de MoS_2 . Este método se distingue por su versatilidad, permitiendo depositar MoS_2 tanto amorfo como cristalino, y su escalabilidad en la manufactura industrial, abarcando desde grosores a nivel nanométrico hasta decenas de nanómetros en diversas arquitecturas. Mediante un código diseñado en *Mathematica*, basado en el Enfoque de Matriz de Transferencia (*TMA*) y las ecuaciones de Fresnel, simulamos las propiedades ópticas y una paleta completa de colores del MoS_2 sintetizado, logrando una notable concordancia con las observaciones experimentales. Gracias a la elección flexible del sustrato, control del grosor, y la posibilidad de recocido o tratamiento térmico establecimos una correlación entre las propiedades ópticas y eléctricas del material. Además, demostramos la eficacia del método al fabricar un metamaterial hiperbólico basado en MoS_2 , simulando inicialmente su estructura multicapa y diagramas de fase con un código de *Mathematica* basado en la Teoría del Medio Efectivo (*EMT*) para así determinar la cantidad de nuestro compuesto para el cual se obtuviese la interesante relación de dispersión hiperbólica, resaltando su potencial en aplicaciones optoelectrónicas avanzadas. En conjunto, nuestro estudio no solo destaca las ventajas multifacéticas de la técnica de deposición propuesta y las mismas tendencias del material reportadas en la literatura para el MoS_2 , sino que también sienta las bases para el desarrollo de dispositivos innovadores a base de MoS_2 .

Palabras Clave: Dicalcogenuros de Metales de Transición (TMDCs), Disulfuro de Molibdeno (MoS_2), Pulverización Catódica Magnetrónica, Tratamiento Térmico, Control de Grosor de Película, Efectos de Tamaño, Enfoque de Matriz de Transferencia (*TMA*), Teoría del Medio Efectivo (*EMT*), Metamaterial Hiperbólico, Propiedades ópticas, Propiedades Eléctricas, Escalabilidad Industrial, Dispositivos Optoelectrónicos, Espectroscopia Raman, Retrodispersión de Rutherford, Ellipsometría, Reflectancia, Difracción de Rayos X, Metodo de cuatro puntos.

Acknowledgements

Al llegar al final de este viaje académico, deseo expresar mi más profundo agradecimiento a aquellas personas que han sido pilares fundamentales en este proyecto y especialmente de mi carrera. Primero, mi especial reconocimiento a mi supervisor, Jose Luis Ocaña Pujol, cuya guía, conocimiento y sabios consejos fueron esenciales en cada etapa del proyecto. Su apoyo incondicional, su trato excepcional, y todo el tiempo dedicado en mi, han sido invaluable, cosas que llevaré conmigo a lo largo de mi vida académica y personal.

Quiero expresar mi gratitud al Instituto Tecnológico de Zürich (ETH Zürich), en particular al Prof. Dr. Ralph Spolenak, por acogerme en su laboratorio y hacerme sentir como parte integral del equipo. Las experiencias compartidas, desde el "Sky Retreat" hasta el "Christmas dinner", han enriquecido enormemente mi estancia. Mis sinceros agradecimientos al Dr. Henning Galinski por sus enriquecedoras conversaciones, ideas innovadoras y su disposición constante para enfrentar los desafíos del proyecto. Quiero agradecer a cada uno de los diferentes miembros del Laboratorio de Nanometalurgia del ETH Zürich, por los almuerzos compartidos, las tasas de café, gratas discusiones en el "Grosslab," y por todo el apoyo y capacitaciones brindadas en los diferentes equipos de laboratorio.

Un agradecimiento especial a mi alma máter, la Universidad del Valle, y a todos los profesores que han compartido su conocimiento y apoyo, tanto académico como personal. En particular, extendiendo mi gratitud a mi supervisor, el Prof. Dr. Germán Antonio Perez Alcazar, por su invaluable apoyo, disposición y orientación en cada aspecto de mi formación. A mis compañeros de universidad, gracias por hacer mi carrera más amena y enriquecedora. Cada conversación y cada momento compartido han sido esenciales en mi crecimiento.

A mi familia, mi padre Ramón Domínguez Cruz, mi madre Carmen Elena Ordóñez Gutierrez, mi hermana Claribel Dominguez Ordóñez y mi cuñado Alessandro Ofner, les agradezco infinitamente su amor, apoyo y dedicación. Su confianza incondicional en mí ha sido la fuente de mi fortaleza y perseverancia. Quiero agradecer profundamente a mi novia Nicolle Peña Bañol por siempre darme su apoyo incluso desde la distancia y motivarme en cada etapa difícil y desafiante que presentaba el proyecto, por siempre apoyar mis sueños y propósitos planteados y por ser mi fan número uno.

Finalmente, agradezco a Dios por sostenerme a lo largo de esta travesía académica. Las enseñanzas éticas y morales del Evangelio de Jesucristo han sido mi guía y fortaleza en los momentos de adversidad, permitiéndome mantenerme firme y enfocado en el propósito por el cual fui creado.

"And ye shall know the truth, and the truth shall make you free."

John 8:32 KJV

Contents

Abstract	i
Acknowledgements	iii
Symbols	vii
1 Introduction	1
1.1 General	1
1.2 Optics And Simulations	4
1.2.1 Wave propagation	4
1.2.2 Explicit E , H , and k for s-polarization and p-polarization . . .	5
1.2.3 Single-interface reflection and transmission amplitudes	6
1.2.4 Ellipsometric parameters	7
1.2.5 The complex refractive index	7
1.3 Effective Medium Theory (EMT)	9
1.4 Multilayer Thin Films	11
1.4.1 Waves coming from both sides	11
1.4.2 Transfer Matrix Approach	12
1.4.3 Metamaterials	15
1.4.4 Hyperbolic Metamaterials (HMMs)	16
1.5 Materials	19
1.5.1 Optical Materials and Electronic Structures	19
1.5.2 2D Transition metal dichalcogenides (2D-TMDCs)	22
Structural Attributes	22
Electronic and Band Structure	24
Synthesis	25
1.5.3 Transition Metal Nitrides (TMNs)	28
1.5.4 Challenges in the Fabrication of Zirconium Nitride (ZrN) . . .	29

1.6	Objective of the Study	31
2	Methods	33
2.1	Film deposition	33
2.1.1	Physical vapor deposition techniques (Sputtering)	33
2.2	Annealing	35
2.3	Optical characterization techniques	36
2.3.1	Raman spectroscopy	36
2.3.2	Ellipsometry	39
2.3.3	Reflectance	40
2.4	Electrical characterization	40
2.4.1	Four point-probe measurement	40
	Method	41
	Rectangular sample	42
	Measurement of body resistivities of thin samples	43
2.5	Design and Mathematica simulations	44
2.6	Additional Characterization Techniques	45
2.6.1	Rutherford Backscattering Spectrometry (RBS)	45
2.6.2	X-Ray Diffraction	45
3	Results and discussion	47
3.1	Raman spectroscopy	47
	Rutherford Backscattering Spectrometry (RBS)	51
	X-Ray Diffraction	53
3.2	Ellipsometry and Reflectance	53
3.2.1	Analysis of the Complex Refractive Index of MoS ₂	53
3.2.2	Analysis of the Optical Properties Of ZrN	56
3.2.3	Reflectance spectrum of MoS ₂ –ZrN composite	59
3.3	Electrical Characterization	60
3.3.1	The temperature-dependent reflectance variation of annealed samples of MoS ₂	62
3.3.2	Resistance and resistivity	62
3.4	Multilayers MoS ₂ –ZrN	66
4	Conclusions and outlook	71
A	Appendix	91

Symbols

Symbols

θ	Angle of incidence
$\mathbf{n}$	Complex refractive index
n, k	Real and imaginary part of $\mathbf{n}$
ε, μ	Permittivity and permeability
$\tilde{\varepsilon}_{eff}, \tilde{\mu}_{eff}$	Effective permittivity and permeability
$\tilde{\varepsilon}', \tilde{\varepsilon}''$ and $\tilde{\mu}', \tilde{\mu}''$	Real and imaginary part of $\tilde{\varepsilon}_{eff}$ and $\tilde{\mu}_{eff}$
$\varepsilon(w), \mu(w)$	Dielectric function and complex permeability
$\varepsilon'(w), \varepsilon''(w)$	Real and imaginary part of $\varepsilon(w)$
$\hat{\varepsilon}, \hat{\mu}$	Effective permittivity and permeability tensor
$\hat{\varepsilon}_{\perp}, \hat{\varepsilon}_{\parallel}$	Out-of-plane and in-plane component of the effective permittivity tensor
f	Filling factor
$\vec{k} = [k_x, k_y, k_z]$	Wavevector
ω, λ	Frequency and wavelength
c	Speed of light in free space
$\vec{E}, \vec{H}$	Electric and magnetic field
$\vec{D}$	Electric displacement
Ψ, Δ	Amplitude component and phase difference in ellipsometry

Acronyms and Abbreviations

ETH	Eidgenössische Technische Hochschule
LNM	Laboratory of Nanometallurgy
EMT	Effective Medium Theory
TMA	Transfer Matrix Approach

Chapter 1

Introduction

1.1 General

In an era dominated by semiconductor technology, optics has emerged as an influential domain, paving the way for advanced optoelectronic devices. Semiconductors, the backbone of numerous modern applications, are at a crossroads where conventional miniaturization endeavors grapple with the physical world's intrinsic limitations Wang et al. (2022). Among the various materials researched for bridging this gap, molybdenum disulfide MoS_2 has risen as a promising contender. This transition metal chalcogenide TMC not only boasts of its sustainability by being composed of relatively abundant and benign elements Gupta et al. (2020), but it also shows an exotic and unique behavior with the tunability of the optical Yu et al. (2015); Lee et al. (2010); Song et al. (2019); Hsu et al. (2019), electrical Siao et al. (2018); Zhao and Ouyang (2019), mechanical Renevier et al. (2000); Rapoport et al. (2008) and electronic Mak et al. (2010); Splendiani et al. (2010); Kuc et al. (2011) properties with thickness.

MoS_2 is a layered material with Molybdenum (M) sandwiched between two Sulfide (S) layers (S–Mo–S). Strong covalent bonds exist between atoms within the crystal, and weak Vander Waals forces exist within layers Yazyev and Kis (2015). This arrangement ensures its application in aerospace machines as a dry lubricant Chiappe et al. (2014). Thinning down bulk crystals of MoS_2 opens the doors to varied electronic and optical attributes in contrast to its bulk counterpart. This transition, resulting from changes in symmetry and structure, transforms an indi-

rect band gap 1.2 eV in bulk to a direct band gap 1.96 eV in monolayers Frey et al. (1998), which made MoS₂ gain popularity because of its band gap unlike graphene in the electronics domain, showcasing spin-orbit effects, marks MoS₂ potential in spintronics and valleytronics. In contrast, its applicability in traditional semiconductor devices like transistors Radisavljevic et al. (2011); Lembke et al. (2015); Kim et al. (2019), LEDs Yang et al. (2021); Hwangbo et al. (2022) and solar cells Tsai et al. (2014); Al-Ghiffari et al. (2022) has also drawn significant attention in the last decade. Among other important applications for MoS₂, we have energy storage and conversion Xue et al. (2017); Yun et al. (2018), as electrodes in sodium Xie et al. (2016) and lithium batteries Feng et al. (2009) and in general optoelectronic devices Zhang et al. (2018).

However, realizing the true potential of MoS₂ requires an efficient and scalable fabrication process. Conventional processes like exfoliation and CVD present challenges in achieving uniform coverage and industrial manufacturing scalability MoS₂, confining the realm of possibilities Xiao et al. (2016); Timpel et al. (2021); Islam and Haque (2021); Kong et al. (2023). Furthermore, these methods predominantly yield crystalline MoS₂, leaving the intriguing domain of amorphous MoS₂ largely unexplored Cao et al. (2017); Krbal et al. (2021). Drawing parallels with the amorphous state of silicon, a-MoS₂ offers properties superior to crystalline counterparts in certain applications, emphasizing the need for a method capable of producing both phases. Another drawback of the current fabrication techniques is that they are only suitable for producing a few nanometers thickness films, leaving the bulk regime relatively unexplored. This is in stark contrast to the wide literature on the thickness dependence of the optical properties of MoS₂, which mostly changes only in thickness ranges accessible by exfoliation and CVD Yazyev and Kis (2015); Islam and Haque (2021); Wang et al. (2022); Splendiani et al. (2010); Lee et al. (2010) which tends to be <10 nm.

The pursuit of alternative fabrication methods compatible with semiconductor processes brings Magnetron Sputtering, a Physical Vapor Deposition technique, to the fore. As a bottom-up technique, it promises deposition of both amorphous and crystalline MoS₂ across a spectrum of thicknesses, spanning from nanoscale to bulk, on diverse substrates Spalvins (1975); Fleischauer (1984); Christy and Ludwig (1979); Muratore et al. (2014); Tao et al. (2015); Ling et al. (2015); Samassekou et al. (2017); Sirota et al. (2019). Like every innovation, magnetron sputtering has its challenges, underscoring the need for real-time feedback in phase and thickness

control and more profound understanding in roughness and grain size.

Two-dimensional materials, like MoS₂, exhibit significant shifts in their properties when they transition between 2D regimes and bulk structures. Understanding the nuances of this transition, be it optical, electrical, mechanical, or electronic, is vital. With many devices and techniques, ranging from ellipsometry to Raman spectroscopy, available to probe and understand these transitions, the journey of discovery and innovation is well-equipped.

In order to showcase advanced architectures involving MoS₂, we will be producing Multilayer Hyperbolic Metamaterials (HMMs). These unique materials exhibit properties that go beyond those of traditional materials Cai and Shalaev (2010). The term "metamaterials" was first introduced by Smith et al. in their study of a composite medium that demonstrated negative permeability and permittivity $\epsilon, \mu < 0$ Smith et al. (2000). HMMs are periodic designer materials that exhibit controllable uniaxial optical anisotropy. This means that the two components of the permittivity tensor can be engineered to have opposite signs, specifically $(\epsilon_{\perp} \cdot \epsilon_{\parallel} < 0)$ Ocana-Pujol et al. (2022). This extreme anisotropy offers unique control over the flow of light energy, resulting in phenomena such as negative refraction Shekhar et al. (2014); Yao et al. (2008); Hoffman et al. (2007), sub-diffraction imaging Jacob et al. (2006); Liu et al. (2007), sub-wavelength modes Govyadinov and Podolskiy (2006); Yao et al. (2011), and thermal emission engineering Guo et al. (2012); Biehs et al. (2012); Nefedov and Simovski (2011). The precise control over optical anisotropy also enables the realization of different dispersion regimes, resulting in optical topological transitions (OTTs) in the isofrequency surface at specific frequencies Ocana-Pujol et al. (2022); Krishnamoorthy et al. (2012). These isofrequency surface topologies are divided into four optical phases or dispersion regimes: effective dielectric ($\epsilon_{\perp} > 0, \epsilon_{\parallel} > 0$), Type I HMM ($\epsilon_{\perp} < 0, \epsilon_{\parallel} > 0$), Type II HMM ($\epsilon_{\perp} > 0, \epsilon_{\parallel} < 0$), and effective metal ($\epsilon_{\perp} < 0, \epsilon_{\parallel} < 0$). These regimes are typically described using Effective Medium Theory (EMT) Cortes et al. (2014).

Our research presents a two-step bottom-up fabrication technique utilizing magnetron sputtering to bridge the gap between the known and unknown realms of MoS₂. By integrating both amorphous and crystalline MoS₂ into advanced architectures and characterizing the functional properties across varying thicknesses and temperatures, this work attempts to elucidate the intertwined relationships between the electrical and optical domain of MoS₂. In doing so, the broader goal remains: harnessing the multifaceted potential of MoS₂ and charting new trajectories for its

application in future optoelectronic devices.

1.2 Optics And Simulations

In the upcoming sections, we will delve into the essential mathematical formulations that form the basis of optics and all the theoretical results to model and fabricate our $\text{MoS}_2\text{--ZrN}$ structures and the $\text{MoS}_2\text{--ZrN}$ HMMs (Section 1.4). For this objective, our work will draw upon the findings previously presented by Byrnes et al. Two Wolfram Mathematica codes use this theory. One code was based purely on the Transfer matrix approach (TMA) (Section 1.4.2) and the Fresnel equations to model the structure and gain control over the optical properties of the $\text{MoS}_2\text{--ZrN}$ structure. The other code combined TMA with Effective Medium Theory (EMT) (Section 1.3). This allowed for parameter optimization of a broader range of parameters and verification that the EMT was valid for our structure. The basics are first reviewed to explain the simulation's theory; then EMT, HMMs, and TMA are explained to simulate further and fabricate our desired composites.

1.2.1 Wave propagation

Our structure consists of one or more smooth planar layers stacked on top of each other. The interfaces between these layers are normal to the $\hat{\mathbf{z}}$ direction, and the structure is uniform in the x and y directions. Assuming that the wavevector of the incident light lies in the $x - z$ plane, we consider the direction of the normally incident incoming light to be $+\hat{\mathbf{z}}$. To obtain the actual value at a specific time, we express all sinusoidally oscillating quantities as complex numbers and multiply by $e^{-i\omega t}$, then take the real part. At any given point, the electric field is a superposition of forward-moving and backward-moving electromagnetic waves, as given by Byrnes (2020); Jackson (1975):

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_f^0 e^{i\mathbf{k}_f \cdot \mathbf{r}} + \mathbf{E}_b^0 e^{i\mathbf{k}_b \cdot \mathbf{r}} \quad (1.1)$$

The values of $\mathbf{k}_f$ and $\mathbf{k}_b$ correspond to the wavevectors for forward and backward waves, respectively. Meanwhile, $\mathbf{E}_f^0$ and $\mathbf{E}_b^0$ are constant vectors, and $\mathbf{E}(\mathbf{r})$ represents the complex electric field at any point $\mathbf{r}$ within a specific layer. Note that the y -components of both $\mathbf{k}_f$ and $\mathbf{k}_b$ are assumed to be zero since the wavevector is in the $x - z$ plane. Moreover, the x -components of $\mathbf{k}_f$ and $\mathbf{k}_b$ are always real, indicating

a plane wave with uniform light intensity along the x and y directions. However, the z -component may be complex, which signifies the attenuation of the wave as it traverses the stack due to absorption Byrnes (2020); Jackson (1975).

The equations for determining the wavevectors are based on the complex index of refraction $\mathbf{n}$ and are as follows Jackson (1975):

$$\mathbf{k}_f = \frac{2\pi\mathbf{n}}{\lambda_{vac}}(\hat{\mathbf{z}} \cos \theta + \hat{\mathbf{x}} \sin \theta) \quad , \quad \mathbf{k}_b = \frac{2\pi\mathbf{n}}{\lambda_{vac}}(-\hat{\mathbf{z}} \cos \theta + \hat{\mathbf{x}} \sin \theta) \quad (1.2)$$

In the equation, θ represents the angle with respect to the normal, and λ_{vac} is the wavelength in vacuum. It is important to note that $n \sin \theta$ is always a real number, whereas $n \cos \theta$ may not be. This is in accordance with Snell's law, which states that $n_i \sin \theta_i = n_j \sin \theta_j$ Hecht (2017). Here, n_i and n_j are the indices of refraction of two different media, while θ_i and θ_j are the corresponding angles of incidence and refraction. In other words, $n \sin \theta$ must remain constant across all layers, equivalent to saying that the component of $\mathbf{k}$ in the $x - y$ plane is uniform throughout the layers.

1.2.2 Explicit $\mathbf{E}$, $\mathbf{H}$, and $\mathbf{k}$ for s-polarization and p-polarization

When light is incident normally on a surface, there is no difference between s-polarization and p-polarization. s-polarization is when the $\mathbf{E}$ -field points in the y -direction, while p-polarization is when the $\mathbf{H}$ -field points in the y -direction. However, due to our sign conventions, we assign opposite signs to the reflection amplitude for normal-incidence waves, depending on whether we label them "s" or "p". For "s"-polarization, our sign convention is based on the direction of the E -field, meaning that if two waves have their E -field pointing parallel, their amplitudes will have the same sign. On the other hand, for p-polarization, our sign convention is based on the direction of the H -field Byrnes (2020); Jackson (1975); Hecht (2017); Zangwill (2013). It is worth noting that half of the textbooks use the opposite sign convention for p Feynman et al. (2011); Griffiths (2013); Lipson et al. (1995) compared to this one, so discrepancies may arise when comparing different sources. For a plane wave, Maxwell's equations imply that $\mathbf{H} = \frac{1}{\mu_0\omega} \mathbf{k} \times \mathbf{E}$, even when $\mathbf{k}$ and/or $\mathbf{E}$ is a complex vector. Therefore, the explicit expressions for $\mathbf{E}$, $\mathbf{H}$, and $\mathbf{k}$ are given by Jackson (1975); Hecht (2017); Zangwill (2013):

s-polarization

$$\begin{aligned}
\mathbf{k}_f &= \frac{2\pi n}{\lambda_{vac}} (\cos \theta \hat{\mathbf{z}} + \sin \theta \hat{\mathbf{x}}) \quad , \quad \mathbf{k}_b = \frac{2\pi n}{\lambda_{vac}} (-\cos \theta \hat{\mathbf{z}} + \sin \theta \hat{\mathbf{x}}) \\
\mathbf{E}_f &= E_f \hat{\mathbf{y}} \quad , \quad \mathbf{E}_b = E_b \hat{\mathbf{y}} \\
\mathbf{H}_f &\propto n E_f (-\cos \theta \hat{\mathbf{x}} + \sin \theta \hat{\mathbf{z}}) \quad , \quad \mathbf{H}_b \propto n E_b (\cos \theta \hat{\mathbf{x}} + \sin \theta \hat{\mathbf{z}})
\end{aligned} \tag{1.3}$$

and

p-polarization

$$\begin{aligned}
\mathbf{k}_f &= \frac{2\pi n}{\lambda_{vac}} (\cos \theta \hat{\mathbf{z}} + \sin \theta \hat{\mathbf{x}}) \quad , \quad \mathbf{k}_b = \frac{2\pi n}{\lambda_{vac}} (-\cos \theta \hat{\mathbf{z}} + \sin \theta \hat{\mathbf{x}}) \\
\mathbf{E}_f &= E_f (-\sin \theta \hat{\mathbf{z}} + \cos \theta \hat{\mathbf{x}}) \quad , \quad \mathbf{E}_b = E_b (-\sin \theta \hat{\mathbf{z}} - \cos \theta \hat{\mathbf{x}}) \\
\mathbf{H}_f &\propto n E_f \hat{\mathbf{y}} \quad , \quad \mathbf{H}_b \propto n E_b \hat{\mathbf{y}}
\end{aligned} \tag{1.4}$$

1.2.3 Single-interface reflection and transmission amplitudes

Let us consider an interface that separates two mediums labeled 1 and 2. When directing light from medium 1 onto this interface, we must consider three significant wave amplitudes: the incident wave amplitude (E_f in medium 1), the reflected wave amplitude (E_b in medium 1), and the transmitted wave amplitude (E_f in medium 2). The ratio of the reflected wave amplitude to the incident wave amplitude is called the reflection coefficient r and the ratio of the transmitted wave amplitude to the incident wave amplitude is called the transmission coefficient t . To derive the Fresnel equations, which give us the equations for r and t , we start with Eqs. (1.3-1.4) applied to both sides of the interface. On the initial side, $E_f = E_0$ and $E_b = rE_0$, while on the terminating side, $E_f = tE_0$ and $E_b = 0$. We then integrate the boundary conditions for the $\mathbf{E}$ and $\mathbf{H}$ vectors, assuming that the components H_x, H_y, H_z, E_x, E_y , and $n^2 E_z$ are consistent across the interface. It is important to note that these boundary conditions apply to the components of the *total* fields $\mathbf{E} = \mathbf{E}_f + \mathbf{E}_b$ and $\mathbf{H} = \mathbf{H}_f + \mathbf{H}_b$. Additionally, we use the fact that B_z and D_z remain consistent across the interface according to Byrnes et al. which can be expressed in terms of H_z and E_z using $\mu = \mu_0, \epsilon = n^2 \epsilon_0$ leads us to the Fresnel equations Byrnes (2020):

$$\begin{aligned}
r_s &= \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \quad , \quad r_p = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_2 \cos \theta_1 + n_1 \cos \theta_2} \\
t_s &= \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \quad , \quad t_p = \frac{2n_1 \cos \theta_1}{n_2 \cos \theta_1 + n_1 \cos \theta_2}
\end{aligned} \tag{1.5}$$

The Fresnel equations establish the relationship between the complex refractive indices $\mathbf{n}$ of two different materials, and the reflection coefficient r and the transmission coefficient t Lipson et al. (1995). Applying these equations makes it possible to determine the Transfer Matrix Approach (Section 1.4.2) for the interface between two materials with known complex refractive indices.

1.2.4 Ellipsometric parameters

Assuming we know the values of r_s and r_t , we can also determine the two parameters measured in ellipsometry. Ellipsometry is a technique that we will discuss in detail in the next chapter (Section 2.3.2). We denote the two parameters as ψ and Δ and calculate them as follows:

$$\psi \equiv \tan^{-1}(|r_p/r_s|) \quad , \quad \Delta \equiv \text{phase}(-r_p/r_s) \tag{1.6}$$

Here, the term "phase" refers to the complex phase angle. However, it is essential to note that the definitions of these parameters may vary across different textbooks. Therefore, it may be necessary to adjust the signs and add or subtract $\pi/2$.

1.2.5 The complex refractive index

The refractive index of an optical medium is a dimensionless quantity that indicates the medium's ability to bend light Hecht (2017). When light passes through a medium, it is also partly absorbed by the material. To account for this absorption, we use a complex refractive index. We define the complex refractive index as Kittel (2005):

$$\mathbf{n} = n + ik \tag{1.7}$$

The real part n represents the refractive index and indicates the phase velocity

of light, while the imaginary part k represents the optical extinction coefficient or absorption coefficient. This coefficient reflects the degree of attenuation or reduction in intensity as an electromagnetic wave propagates through the material. A higher extinction coefficient indicates faster absorption, while a negative extinction coefficient corresponds to stimulated emission Byrnes (2020).

The electromagnetic properties of a material are determined by two material parameters: The permittivity ϵ and the permeability μ , describing the coupling of a material to the electric and magnetic field components of an electromagnetic wave, respectively. We define the refractive index n with the following equation Cai and Shalaev (2010):

$$n = \sqrt{\epsilon\mu} \quad (1.8)$$

The simple square-root relationship between the refractive index and the permittivity still holds in the frequency domain. Extending our "real" domain to include complex counterparts is crucial to accurately capturing our system's inherent energy losses or gains. This includes absorption, amplification, and scattering processes. By accounting for these imaginary components, our understanding and ability to predict wave-material interactions would be complete. Most naturally occurring materials exhibit negligible magnetism at optical frequencies, with μ approximating 1. Therefore, the complex refractive index $\mathbf{n}$ is related to the dielectric function by $\mathbf{n} = \sqrt{\epsilon(w)} = n + ik$ Cai and Shalaev (2010). Some algebra leads us to the useful relations between the real and imaginary parts of the complex refractive index and those of the complex dielectric function ($\epsilon(w) = \epsilon'(w) + i\epsilon''(w)$) Cai and Shalaev (2010); Maier (2007); Kittel (2005):

$$\epsilon' = n^2 - k^2; \quad \epsilon'' = 2nk \quad (1.9)$$

$$n^2 = \left[\epsilon' + \frac{\sqrt{\epsilon'^2 + \epsilon''^2}}{2} \right]; \quad k^2 = \left[-\epsilon' + \frac{\sqrt{\epsilon'^2 + \epsilon''^2}}{2} \right]; \quad (1.10)$$

We omit the argument ω to make the equations concise. Although in Section 1.5, we will explore the optical and electronic properties of metals and dielectrics,

we would like to define them in terms of the dielectric function briefly. A metal is a material highly reflective to electromagnetic waves for frequencies up to the optical region ($\epsilon' = n^2 - k^2 < 0$), whereas dielectrics are transparent to them ($\epsilon' > 0$) Maier (2007); Jackson (1998); Ashcroft and Mermin (1976); Kittel (2005); Yang et al. (2020)

1.3 Effective Medium Theory (EMT)

When metal and dielectric components are mixed disorderly in a composite, the system's boundary conditions become so complex that solving Maxwell's equations to determine its electromagnetic response becomes practically impossible. However, we can simplify the situation significantly under certain conditions.

When we study a system with a composite system characterized by an inhomogeneity scale much smaller than the wavelength of interest, the electrodynamic scattering caused by individual metal or dielectric particles becomes insignificant when compared to the overall response of the entire system Cai and Shalaev (2010). Consequently, the optical properties of a microscopically heterogeneous composite can be studied by analyzing the effective dielectric function of a macroscopically uniform medium Cai and Shalaev (2010).

To determine the effective dielectric function of a composite material, one can use the permittivities of its individual components and their corresponding volume fractions. This approach, also known as the effective medium theory (EMT), simplifies understanding the composite's optical behavior. Among various mean-field theories, Bruggeman's effective medium theory is perhaps the most well-known Bruggeman (1935). According to Bruggeman's theory, a disordered composite with two interpenetrating components having permittivities ϵ_1 and ϵ_2 can be related to an effective medium with the permittivity $\tilde{\epsilon}_{eff}$, which represents the composite material itself Bruggeman (1935).

$$f_1 \frac{\epsilon_1 - \tilde{\epsilon}_{eff}}{\epsilon_1 + 2\tilde{\epsilon}_{eff}} + f_2 \frac{\epsilon_2 - \tilde{\epsilon}_{eff}}{\epsilon_2 + 2\tilde{\epsilon}_{eff}} = 0 \quad (1.11)$$

The equation above involves volume filling factors denoted by f_1 and f_2 , satisfying the condition $f_1 + f_2 = 1$. The equation has two possible solutions; one is discarded due to having a negative imaginary part of $\tilde{\epsilon}_{eff}$ Bruggeman (1935). In the EMT proposed by Bruggeman, the two components within the composite are

symmetrical in terms of their roles. This means that both phases are treated as embedded in the effective medium, and there is no need to prioritize one phase over the other Cai and Shalaev (2010).

Figure 1.3 **a)** (Section 1.4) depicts a multilayer structure formed by alternating metallic and dielectric layers, resulting in anisotropic effective permittivity. Here, metallic and dielectric layers have permittivities of ϵ_m and ϵ_d , respectively. The fill fraction, represented by ρ , is defined as the ratio of the total metallic layer thickness (t_m) to the total thickness of the composite, given by the equation $\rho = \frac{t_m}{t_m + t_d}$ Shekhar et al. (2014). In this equation, t_m and t_d denote the total thicknesses of the metallic and dielectric layers, respectively, collectively referred to as a metamaterial (refer to Section 1.4.3).

To derive the effective medium permittivities of our composite with a uniaxial symmetry we follow a generalized Maxwell-Garnett Garnett and Larmor (1997a,b) approach and the interpretations made by Shekhar et al. to obtain analytical expressions for the effective permittivity in the parallel ($\tilde{\epsilon}_{\parallel}$) and perpendicular ($\tilde{\epsilon}_{\perp}$) directions Shekhar et al. (2014)

To derive the analytical expression for the parallel component of the permittivity tensor for our multilayer system, we start by noting the direct proportionality between the electric field displacement ($\vec{D}$) and the electric field ($\vec{E}$), expressed as $\vec{D} = \tilde{\epsilon}_{eff} \vec{E}$. Here, $\tilde{\epsilon}_{eff}$ denotes the medium's overall effective permittivity. Given the continuity of the tangential component of the electric field across interfaces between mediums, we establish that $E_m^{\parallel} = E_d^{\parallel} = E^{\parallel}$ Shekhar et al. (2014). In this notation, $E_m^{\parallel}$, $E_d^{\parallel}$, and $E^{\parallel}$ represent the electric fields within metallic layers, dielectric layers, and the subwavelength metamaterial, respectively. By considering the continuity of dielectric displacement in the parallel direction, the overall displacement can be determined by averaging the displacement field contributions from both metallic and dielectric components: $D^{\parallel} = \rho D_m^{\parallel} + (1 - \rho) D_d^{\parallel}$. This leads to the equation: $\tilde{\epsilon}_{eff}^{\parallel} E^{\parallel} = \rho \epsilon_m E^{\parallel} + (1 - \rho) \epsilon_d E^{\parallel}$. Upon canceling out the electric field components, we obtain the following result Shekhar et al. (2014):

$$\tilde{\epsilon}_{eff}^{\parallel} = \rho \epsilon_m + (1 - \rho) \epsilon_d \quad (1.12)$$

Substituting ρ , the following equation in terms of the thicknesses of the components holds Poddubny et al. (2013):

$$\tilde{\epsilon}_{\parallel} = \frac{\epsilon_m t_m + \epsilon_d t_d}{t_m + t_d} \quad (1.13)$$

To derive the perpendicular permittivity expression for our multilayer system, we start with Maxwell's equations and apply electromagnetic field boundary conditions. It is established that the normal component of the electric displacement vector remains continuous at an interface, leading to $D_m^{\parallel} = D_d^{\parallel} = D^{\parallel}$. The total electric field magnitude, $E^{\perp}$, can be expressed as a superposition of the electric field components within the dielectric ($E_d^{\perp}$) and metallic layers ($E_m^{\perp}$), given by the relation: $E^{\perp} = \rho E_m^{\perp} + (1 - \rho) E_d^{\perp}$. Applying the electric displacement boundary condition and Maxwell's equations, and then isolating $\tilde{\epsilon}_{\perp}$, we derive the analytical expression for the multilayer metamaterial's perpendicular electric permittivity, expressed both in terms of the filling fraction and the components' thicknesses Shekhar et al. (2014); Poddubny et al. (2013):

$$\tilde{\epsilon}_{\perp} = \frac{\epsilon_m \epsilon_d}{\rho \epsilon_d + (1 - \rho) \epsilon_m} \quad (1.14)$$

$$\tilde{\epsilon}_{\perp} = \epsilon_m \epsilon_d \frac{t_m + t_d}{t_m \epsilon_d + t_d \epsilon_m} \quad (1.15)$$

For structures with more than two material layers ($n \geq 2$), the formulas can be generalized:

$$\tilde{\epsilon}_{\parallel} = \frac{\sum_{i=1}^n l_i \epsilon_i}{\sum_{i=1}^n l_i} \quad (1.16)$$

$$\tilde{\epsilon}_{\perp} = \frac{\sum_{i=1}^n l_i}{\sum_{i=1}^n \frac{l_i}{\epsilon_i}} \quad (1.17)$$

1.4 Multilayer Thin Films

1.4.1 Waves coming from both sides

An interesting modification of the scenario presented in Section 1.2.3 involves waves simultaneously arriving from both sides of the interface. The amplitudes of these waves are represented as E_{f1} , E_{b1} , E_{f2} , and E_{b2} , which respectively denote forward

direction in medium 1, backward in medium 1, forward in medium 2, and backward in medium 2. The equations show the relationship between these amplitudes and can be expressed as Byrnes (2020):

$$E_{b1} = E_{f1}r_{12} + E_{b2}t_{21} \quad , \quad E_{f2} = E_{f1}t_{12} + E_{b2}r_{21} \quad (1.18)$$

Here, t_{ab} and r_{ab} represent the transmission and reflection values for the wave transitioning from layer a to b . The intuitive understanding of these relationships is that each outgoing wave combines the reflected amplitude of one of the incoming waves and the transmitted amplitude of the other incoming wave Byrnes (2020).

Although these equations can be derived from electromagnetic boundary conditions, it is simpler to understand that two situations comply with these boundary conditions: $(E_{f1}, E_{b1}, E_{f2}, E_{b2}) = (1, r_{12}, t_{12}, 0)$ and $(0, t_{21}, r_{21}, 1)$. Since both of these sets meet the boundary conditions expressed in equation 1.18, it implies that any linear combination or superposition of these two sets - which encapsulates all potential combinations of incoming waves - would also satisfy these conditions Byrnes (2020).

1.4.2 Transfer Matrix Approach

The transfer matrix $\mathbf{M}$ connects the wave function on the right side of a sample to that on the left side. In contrast, the scattering matrix $\mathbf{S}$ relates incoming waves from both sample sides to outgoing waves. One can compute the transfer matrix using the reflection and transmission amplitudes Markoš and Soukoulis (2008). As elaborated in Section 1.2.3, the Fresnel equations associate the complex refractive indices, n , of two materials with the reflection coefficient, r , and transmission coefficient, t . Hence, it is feasible to determine the transfer matrix for the interface between two materials with known refractive indices.

Let us consider that we are dealing with N different materials, indexed from 0 to $N - 1$, the first and last materials, respectively, which are semi-infinite. A light wave with amplitude 1 starts from the $0th$ layer and heads towards the $1st$ layer (as shown in Figure. 1.1).

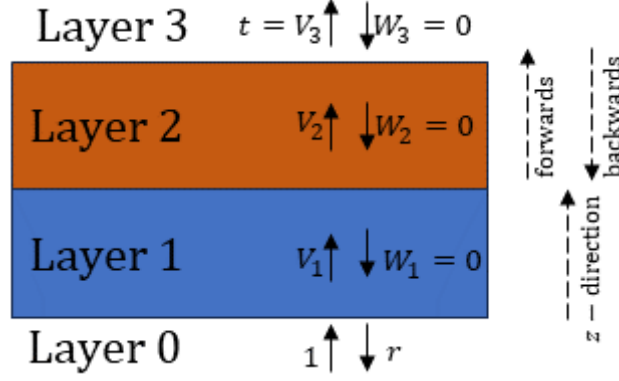


Figure 1.1 – Sample stack with $N = 4$ (two finite layers between two semi-infinite layers). The labels next to the small arrows indicate wave amplitudes.

When light encounters the boundary between the $(n - 1)$ st and n th material, we denote the wave's amplitude on the n th side (moving away from the boundary) as v_n . Conversely, w_n represents the wave's amplitude moving in the opposite direction, i.e., towards the boundary, on the n th side (as shown in Figure . 1.1). Here, (v_0, w_0) are not defined, but $v_{N-1} = t$ and $w_{N-1} = 0$. We define Byrnes (2020):

$$\delta_n \equiv (\text{thickness of layer } n)(k_z \text{ for the forward-traveling wave in layer } n) \quad (1.19)$$

Thus, δ_n encapsulates the phase shift (and absorption if k_z is complex) resulting from the wave's traversal through layer n . From Equation (1.18) we obtain:

$$\begin{aligned} v_{n+1} &= (v_n e^{i\delta_n}) t_{n,n+1} + w_{n+1} r_{n+1,n} \\ w_n e^{-i\delta_n} &= w_{n+1} t_{n+1,n} + (v_n e^{i\delta_n}) r_{n,n+1} \end{aligned} \quad (1.20)$$

$r_{a,b}$ and $t_{a,b}$ represent the reflection and transmission of light moving from layer a to layer b respectively. We can transform these using the identities $r_{a,b} = -r_{b,a}$ and $t_{a,b} t_{b,a} - r_{a,b} r_{b,a} = 1$ which can be derived from *Fresnel equations* (Eqs 1.5) into Byrnes (2020):

$$\begin{pmatrix} v_n \\ w_n \end{pmatrix} = M_n \begin{pmatrix} v_{n+1} \\ w_{n+1} \end{pmatrix} \quad (1.21)$$

This holds for $n = 1, \dots, N - 2$, with $M_n = \mathbf{P}_n \mathbf{M}_{n,n+1}$

$$\mathbf{P}_n \mathbf{M}_{n,n+1} \equiv \begin{pmatrix} e^{-i\delta_n} & 0 \\ 0 & e^{i\delta_n} \end{pmatrix} \begin{pmatrix} 1 & r_{n,n+1} \\ r_{n,n+1} & 1 \end{pmatrix} \frac{1}{t_{n,n+1}} \quad (1.22)$$

The transfer matrix $\mathbf{M}_{n,n+1}$ is then responsible for connecting the wave function on the right-hand side of a sample with the wave function on the left-hand side. Additionally, since the electromagnetic wave must propagate from one interface to the next, an additional matrix called the propagator $\mathbf{P}_n$ is required. As stated earlier, we can see how the transfer matrix can be computed from the reflection and transmission amplitudes Markoš and Soukoulis (2008).

Now we want the matrix relating the waves entering the structure to the waves exiting, i.e.:

$$\begin{pmatrix} 1 \\ r \end{pmatrix} = \tilde{M} \begin{pmatrix} t \\ 0 \end{pmatrix}. \quad (1.23)$$

Several transfer matrices must be multiplied in a layered medium with multiple interfaces. The matrix $\tilde{M}$ is expressed as Byrnes (2020):

$$\tilde{M} = \frac{1}{t_{0,1}} \begin{pmatrix} 1 & r_{0,1} \\ r_{0,1} & 1 \end{pmatrix} M_1 M_2 \cdots M_{N-2} \quad (1.24)$$

By combining these two equations, r and t can be represented in terms of the four entries of the matrix $\tilde{M}$ Byrnes (2020):

$$\begin{pmatrix} 1 \\ r \end{pmatrix} = \begin{pmatrix} \tilde{M}_{00} & \tilde{M}_{01} \\ \tilde{M}_{10} & \tilde{M}_{11} \end{pmatrix} \begin{pmatrix} t \\ 0 \end{pmatrix} \quad (1.25)$$

$$t = 1/\tilde{M}_{00}, \quad r = \tilde{M}_{10}/\tilde{M}_{00} \quad (1.26)$$

Hence, we have a method to calculate r and t for any given multi-layer thin film. Calculating v_n and w_n for each layer n from here is also straightforward. By multiplying the propagator and transfer matrices, it is possible to obtain the overall reflection and transmission amplitude, as well as the ellipsometric parameters Ψ

and Δ as shown in the Section 1.2.4 Byrnes (2020), Harbecke (1986), Katsidis and Siapkis (2002).

1.4.3 Metamaterials

Electromagnetic devices and phenomena are fundamentally shaped by the interaction between waves and materials Cai and Shalaev (2010). Although the range of electromagnetic devices has expanded due to various sophisticated structures developed globally, their capabilities are still fundamentally constrained by the available materials. There are inherent limitations that prevent specific desired properties from manifesting. For instance, due to the causality requirement, no medium can propel optical pulses faster than light's speed in a vacuum. Curiously, while not forbidden by physical laws, specific electromagnetic properties, analogous to monopole magnets, appear absent in nature Cai and Shalaev (2010).

The term "metamaterial" originates from the Greek prefix "meta" ($\mu\epsilon\tau\alpha$), meaning "beyond," signifying systems surpassing conventional materials. It was first coined in 2000 by Smith et al. upon introducing a material with negative permeability and permittivity at microwave frequencies Smith et al. (2000). Since then, the use of "metamaterial" has proliferated, but a consensus on its definition remains elusive, with existing descriptions not universally accepted among researchers in the field. Metamaterials are, above all, man-made materials Cai and Shalaev (2010).

We would attain the definition stayed by Cai and Shalaev *et al* for our discussions: *"A metamaterial is an artificially structured material which attains its properties from the unit structure rather than the constituent materials. A metamaterial has an inhomogeneity scale that is much smaller than the wavelength of interest, and its electromagnetic response is expressed in terms of homogenized material parameters"* Cai and Shalaev (2010). This definition captures the essence of the metamaterial: The structural units of a metamaterial, known as meta-atoms or meta-molecules, must be substantially smaller than the wavelength being considered, and the average distance between neighboring meta-atoms is also subwavelength in scale, giving rise to those unique properties Cai and Shalaev (2010). Within the rapidly developing and highly multidisciplinary field of optical metamaterials, several key research directions have been emerging, including sub-diffraction imaging Jacob et al. (2006); Liu et al. (2007), engineering and tuning of spontaneous emission Iorsh et al. (2012), invisibility devices Pendry et al. (2006); Cai et al. (2007), waveguiding Govyadinov and Podolskiy (2006); Podolskiy and Narimanov (2005),

perfect absorbers Liu et al. (2011), resonators at the nanoscale Jahani and Jacob (2016) and negative refraction materials Hoffman et al. (2007); Yao et al. (2008). Out of the various metamaterials, hyperbolic metamaterials (HMMs) have been a rapidly emerging field in nanophotonics due to their extremely high anisotropy with a hyperbolic dispersion relation Lee et al. (2022).

1.4.4 Hyperbolic Metamaterials (HMMs)

Hyperbolic metamaterials (HMMs) are named after the topology of their isofrequency surface Shekhar et al. (2014). When a material is isotropic in vacuum, it exhibits linear dispersion, resulting in a spherical isofrequency surface (as shown in Figure 1.2a). This spherical surface represents the isotropic propagation of waves, such as light, sound, or heat waves, and is given by the equation Lee et al. (2022):

$$k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{c^2} \quad (1.27)$$

The wave vector $\vec{k} = [k_x, k_y, k_z]$ represents the direction and magnitude of the wave propagation along the x , y , and z axes, respectively. The angular frequency is denoted by ω , and c represents the speed of light in free space.

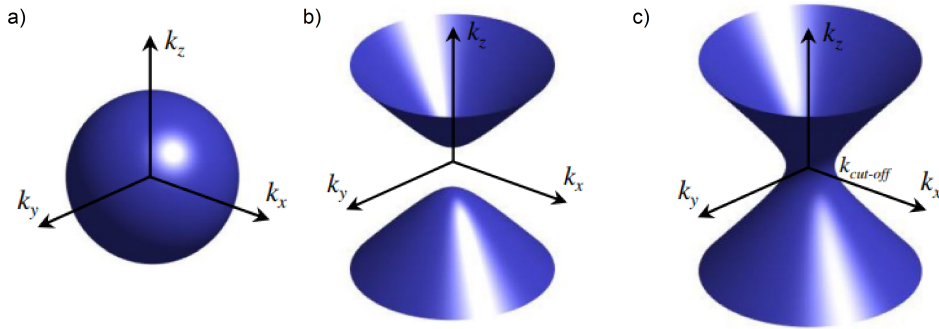


Figure 1.2 – Isofrequency contours. Isofrequency contours for **a)** an isotropic medium, **b)** a dielectric-type hyperbolic metamaterial (HMM), and **c)** a metallic-type HMM. Adapted from Lee et al. (2022)

The permittivity tensor $\hat{\epsilon}$ and permeability tensor $\hat{\mu}$ of the material, when aligned with the principal axes, are defined as Lee et al. (2022)

$$\hat{\epsilon} = \epsilon_0 \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix} \quad \hat{\mu} = \mu_0 \begin{pmatrix} \mu_{xx} & 0 & 0 \\ 0 & \mu_{yy} & 0 \\ 0 & 0 & \mu_{zz} \end{pmatrix} \quad (1.28)$$

Here, ϵ_0 and μ_0 represent permittivity and permeability in a vacuum, respectively, determining how electric and magnetic fields interact with the material. Typically, materials are *isotropic*, exhibiting equal permittivity and permeability in all directions ($\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$, $\mu_{xx} = \mu_{yy} = \mu_{zz}$). The material is identified as a uniaxial or biaxial anisotropic medium if these principal components vary. With the optical axis (OA) aligned along the z-direction, an electric uniaxial medium presents $\epsilon_{xx} = \epsilon_{yy} \neq \epsilon_{zz}$, while a magnetic uniaxial medium displays $\mu_{xx} = \mu_{yy} \neq \mu_{zz}$. An electric biaxial medium, on the other hand, has $\epsilon_{xx} \neq \epsilon_{yy} \neq \epsilon_{zz}$, and a magnetic biaxial medium exhibits $\mu_{xx} \neq \mu_{yy} \neq \mu_{zz}$ Lee et al. (2022). We will consider an electric uniaxial material exposed to transverse magnetic (TM) (p – *polarized*) polarized light for simplicity. The dispersion relation in this medium, with effective permittivity as in Eq. 1.28, can be derived from Maxwell's equations as Lee et al. (2022).

$$\frac{k_x^2 + k_y^2}{\epsilon_{zz}} + \frac{k_z^2}{\epsilon_{xx}} = \frac{\omega^2}{c^2} \quad (1.29)$$

The isofrequency contour (IFC) in Eq.(1.29) is derived from the intersection between the constant frequency plane and the dispersion surface Lee et al. (2022). In anisotropic media, the components of the permittivity tensor, ϵ , are non-uniform, characterized by in-plane components $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{\parallel}$ and the out-of-plane component $\epsilon_{zz} = \epsilon_{\perp}$. In conventional materials, effective permittivity components share the same sign, yielding a closed, IFC-typically a sphere or ellipsoid (see Figure 1.2 a)). This closed IFC limits the propagation of waves with large wave vectors in these materials. However, when permittivity components have opposite signs ($\epsilon_{zz} \cdot \epsilon_{xx} = \epsilon_{\perp} \cdot \epsilon_{\parallel} < 0$), the IFC evolves into an unbounded hyperboloid, supporting high- k waves Poddubny et al. (2013); Shekhar et al. (2014); Ferrari et al. (2015), achieving such extreme anisotropy in the permittivity tensor is possible with a composite of metal and dielectric components, structured with subwavelength feature size, while rare in nature, these materials can be artificially developed through metamaterials (Section 1.4.3), described as a single medium with anisotropic permittivity

by the Effective Medium Theory (EMT) (Section 1.3).

HMMs can be classified into two types based on the sign of their permittivity components. When $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{\parallel} > 0$ and $\epsilon_{zz} = \epsilon_{\perp} < 0$, the material exhibits a predominantly dielectric nature and is referred to as Type-I HMMs (Figure 1.2 **b**)) Lee et al. (2022). On the other hand, when $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{\parallel} < 0$ and $\epsilon_{zz} = \epsilon_{\perp} > 0$, the material exhibits more metallic properties and is known as Type-II HMMs (Figure 1.2 **c**)) Lee et al. (2022). Due to their predominantly metallic nature, Type-II HMMs show high absorption properties and support high- k waves only up to a cut-off spatial frequency Lee et al. (2022). The Type I and Type II hyperbolic metamaterials exhibit distinct differences. Specifically, the hyperboloidal surfaces of Type I metamaterial are two-sheeted, while Type II metamaterial is single-sheeted Shekhar et al. (2014). Additionally, the reflective properties of the Type II metamaterial surpass those of Type I due to its higher metallic composition Korobkin et al. (2010). Figure 1.2b) shows how the Type I possesses a band gap in the isofrequency surface, thus being less reflective and more transmitting than Type II. Therefore, one can also call Type I the *dielectric type* and Type II the *metallic type*. Note that if all components are negative, we obtain a metal; we will have a dielectric medium if all components are positive.

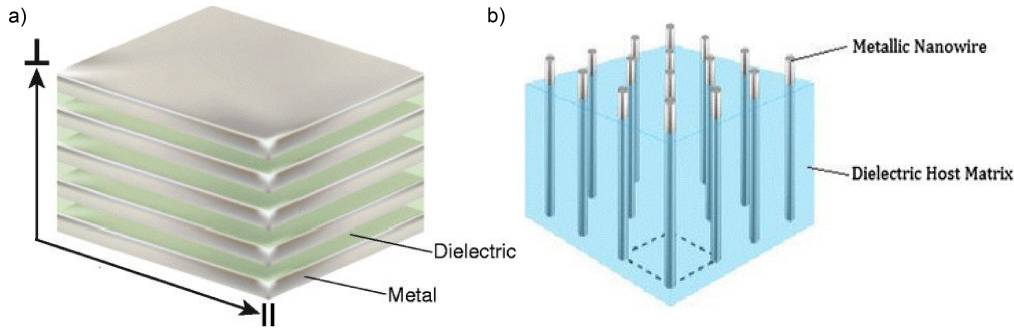


Figure 1.3 – **a)** Multilayer structure consisting of alternating metallic and dielectric layers forming a metal-dielectric superlattice. **b)** Nanowire structure consisting of metallic nanorods embedded in a dielectric host. In both **b)** and **c)**, the constituent components are subwavelength, allowing characterization with EMT. Adapted from Shekhar et al. (2014)

There are two viable methods for achieving hyperbolic dispersion: a metal-dielectric superlattice, which involves a multilayer structure with alternating metallic and dielectric layers (Figure 1.3 **a**)), and a nanowire structure that incorporates metallic nanorods within a dielectric host (Figure 1.3 **b**)). In this work, the geometry

of a periodic multilayer was used.

1.5 Materials

Until this point, we have laid the groundwork with the necessary mathematical constructions that sustain the content of this work. As we delve deeper into our study, it becomes essential to introduce a dedicated section that focuses on the materials at hand, their intricate structures, electronic properties, and band structures. Furthermore, we will delve into the synthesis methodologies employed for obtaining these metamaterials, providing valuable insights into the experimental challenges in our investigation.

1.5.1 Optical Materials and Electronic Structures

In order to design and implement optical metamaterials, it is essential to study the physical properties of the primary constituent materials, including dielectrics, semiconductors, and metals. It is also necessary to understand the mechanism responsible for their optical behaviors.

Although used extensively in optics, the terms "*dielectric*" and "*metals*" are borrowed from electronics, where different types of bulk materials are classified based on their resistivity Cai and Shalaev (2010). Metals exhibit high electrical conductivity. Many electrons are free to move in metals, usually one or two per atom when an electric potential difference is applied to the material Kittel (2005). The electrons available to move about are called conduction electrons. The valence electrons of the atom become the conduction electrons of the metal. Metals are the most commonly used conductors since they are rich in loosely held free electrons because one or more of their energy bands are partly filled Cai and Shalaev (2010). In a dielectric, also called an insulator, the allowed energy bands are either filled or empty Cai et al. (2007); all charges are attached to specific atoms or molecules Griffiths (2013). As a result, they prevent electron movement in an electric field, and the flow of electric current is prohibited. Notice that even insulators conduct slightly, though the conductivity of a metal is astronomically more excellent; for most purposes, metals can be regarded as perfect conductors, with $\sigma = \infty$ while for insulators, we can pretend $\sigma = 0$, where σ is an empirical constant, it is called the conductivity of the medium Griffiths (2013). Another important category in the electronic material classification system is "*semiconductors*", which are materials that have all their energy bands

filled except for one or two bands that are slightly filled or empty Cai and Shalaev (2010). One can distinguish between these electronic materials using the Fermi level and energy band theory, commonly explained in solid state physics textbooks Kittel (2005); Ashcroft and Mermin (1976).

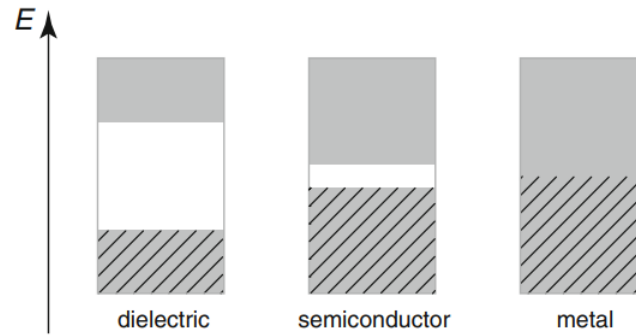


Figure 1.4 – Simplified energy band diagram for a typical dielectric, semiconductor, and metal. The shaded and light gray regions represent the valence and conduction bands, respectively, and the empty region between them indicates the band gap. Adapted from Cai and Shalaev (2010).

According to the Pauli exclusion principle, no two electrons in an atom can share one identical quantum state Pauli (1925). Interestingly, this notion of discreteness extends beyond just individual atomic systems. For example, discrete energy levels are created in a crystalline solid due to the covalent bonding of atoms in the crystal lattice Cai and Shalaev (2010). These allowed energy levels are grouped into two distinct bands: the *conduction band* and the *valence band*. The valence band has many closely spaced levels filled mainly by electrons, while the conduction band represents electronic levels at higher energies that are mostly unoccupied. The two bands are separated by an energy region where no electron states are allowed. The width of this empty energy region, called a *band gap* or forbidden band, determines whether a substance is a dielectric, semiconductor, or conductor Cai and Shalaev (2010). The band gap is the energy difference between the conduction band's lowest point and the valence band's highest point Kittel (2005). The band gap width represents the energy barrier that must be overcome by a bound electron in the valence band in order to take part in the electric conduction process Cai and Shalaev (2010). The energy band diagrams for typical dielectrics, semiconductors, and metals are illustrated in Figure 1.4. In conductors like metals, the valence and conduction bands overlap without a forbidden band in between. Consequently, any energy added to electrons is sufficient to propel them into the conduction band Cai and Shalaev (2010). A vast energy band gap characterizes a dielectric; a significant

energy boost is required to move an electron from the valence band to the conduction band. The band structure of semiconductors, as shown in the middle of the panel in Figure 1.4, is probably the most familiar band diagram because of the extensive use of semiconductors in today's electronics industry. The moderate forbidden gap allows electrons in the valence band to be lifted to the conduction band with a small excitation energy and becomes accessible to conduct current.

We can distinguish two forbidden band gaps without entering unnecessary details in this work. One type emerges when the lowest-energy state in the conduction band and the highest-energy state in the valence band are situated at the exact location of the Brillouin zone (i.e., they share the same k -vector) Rosencher and Vinter (2002), we will see the transition occurring at constant k , the corresponding energy gap is referred as being *direct*. If the k -vectors differ, the material has an *indirect gap* Rosencher and Vinter (2002). In other words, the band gap is called *direct* when the crystal momentum for both electrons and holes aligns in the conduction and valence bands, i.e., GaAs; an electron can directly emit a photon. In an indirect gap, a photon is not emitted since the electron transitions via an intermediary stage, imparting momentum to the crystal structure, i.e., Silicon Rosencher and Vinter (2002).

We should be cautious when applying the concepts from electronics to our optical studies. Many dielectrics have their optical properties tightly linked to their electronic structures. For instance, visible light's photon energy, between 1.5 eV and 3 eV, does not bridge the gap between the valence and conduction bands in most insulators, making them transparent Cai and Shalaev (2010). It is tempting to categorize materials purely by their electronic features, but this can mislead. For example, indium tin oxide (ITO) is electronically metal-like but optically behaves as a dielectric Cai and Shalaev (2010). Similarly, tungsten conducts in light bulb filaments but, in the visible spectrum, acts more like a lossy dielectric Cai and Shalaev (2010).

This intricate relationship between electronic and optical properties becomes particularly evident when considering how materials interact with light. As explored in Section 1.2.5, the optical definitions of metals and dielectrics dictate these interactions. Materials' electronic structures influence their response to different light wavelengths, affecting our color perception. The dielectric function of a material serves as a keystone in this relationship, elucidating the mechanisms behind the colors a material exhibits. Color perception arises from the nuanced interactions

of various wavelengths in white light with matter, whether through absorption, reflection, refraction, scattering, or diffraction Nassau (1987). A prime illustration is gold: its dielectric function, influenced by its electronic structure, deviates towards the positive $\epsilon(w)$ direction (more dielectric-like). This causes heightened absorption of blue and green light, revealing the metal’s characteristic yellow tone as the dominant reflected color to an observer Cai and Shalaev (2010).

1.5.2 2D Transition metal dichalcogenides (2D–TMDCs)

Graphene is the most extensively studied two-dimensional material Novoselov et al. (2004), while graphene boasts remarkable properties, both because of its rich physics Novoselov et al. (2005) and high mobility Bolotin et al. (2008), its lack of an electronic band gap has driven research towards alternative 2D materials Ferrari et al. (2006); Geim and Novoselov (2007). Transition Metal Dichalcogenides (TMDCs) are layered materials with strong in-plane bonding and weak out-of-plane interaction that can be obtained through exfoliation of bulk materials or bottom-up syntheses Wang et al. (2012); Chhowalla et al. (2013). TMDCs are expressed as (MX_2) , where M is a transition metal and X a chalcogen, have emerged as promising candidates Manzeli et al. (2017). In contrast to the graphene sheets, these materials are chemically versatile, and their electronic properties can be tailored based on composition and layering Chhowalla et al. (2013). Notably, TMDCs like MoS_2 , $MoSe_2$, WS_2 , and WSe_2 transition from an indirect to a direct band gap when reduced to single layers, making them ideal for various optoelectronic applications Wang et al. (2012).

In the realm of TMDCs, MoS_2 is a semiconductor of significant interest. MoS_2 , has been shown to have high mobility in single-layer transistor configurations, comparable to graphene nanoribbons Radisavljevic et al. (2011). Such attributes, combined with a direct band gap in monolayer MoS_2 , its inherent robustness, and abundance underscore its potential in applications such as optoelectronics and energy harvesting, complementing graphene’s capabilities Radisavljevic et al. (2011); Chhowalla et al. (2013).

Structural Attributes

TMDCs present intricate structural facets that are instrumental in determining their distinctive electronic and optical characteristics. At the atomic level, TMDCs are composed of a central hexagonally packed layer of transition metal atoms, flanked on either side by layers of chalcogen atoms, yielding an X–M–X configuration Wang

et al. (2012). The bonds within these layers are predominantly covalent, and weak van der Waals forces govern the coupling between adjacent layers. This unique combination of bonding allows for easy exfoliation similar to graphite Chhowalla et al. (2013).

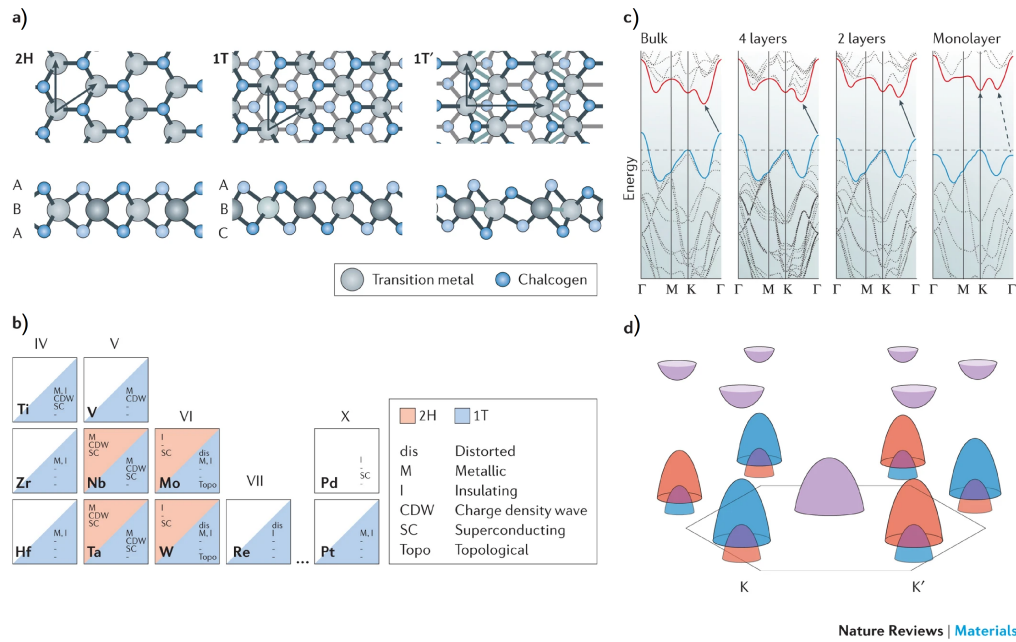


Figure 1.5 – a) Atomic structure of single-layer TMDCs in their trigonal prismatic (2H), distorted octahedral (1T), and dimerized (1T') phases, detailing lattice vectors and plane stacking. b) "Periodic table" of layered TMDCs, categorized by transition metal, outlining phases such as 2H, 1T, and unique phases for metals like Pd. c) Changes in band structure of 2H–MoS₂ as thickness diminishes. d) Schematic of monolayer 2H–MoS₂ band structure, with spin splitting at the K and K' Brillouin zone points. Orange and blue signify up and down spin, respectively. Adapted from Manzeli et al. (2017)

Two pivotal structural phases characterize TMDCs: the trigonal prismatic (2H) and the octahedral (1T) coordination (Figure 1.5 a)). In the 2H phase, there is an ABA stacking sequence, wherein chalcogen atoms across different planes occupy identical positions. Contrarily, the 1T phase embodies an ABC stacking order Manzeli et al. (2017). The thermodynamically stable phase for a specific TMDC depends upon the specific combination of the transition metal (ranging from groups IV to X) and the chalcogen element (like S, Se, or Te). It is important to note that while one phase might be thermodynamically stable, the other can sometimes exist as a metastable phase—a state that may change over time, although slowly (Figure 1.5 b)) Manzeli et al. (2017). In materials science, a *stable* equilibrium describes a

state wherein a material remains unchanged indefinitely, typically corresponding to its lowest energy configuration. Conversely, a *metastable* state represents a condition that, although not in its most stable form, persists without observable changes over extended periods due to its slow transformation rate Wood and Anderson (2014).

These basic stacking configurations further diversify for multilayer and bulk TMDC samples, and their structure can undergo distortions, diminishing the periodicity. In some cases, such distortions can even induce the formation of metal-metal bonds, leading to the emergence of new phases, such as the 1 T' phase in some TMDCs Manzeli et al. (2017).

In a more holistic perspective, TMDCs crystallize in a layered structure similar to graphite. Interestingly, a specific TMDC can exist in multiple such structural configurations, contingent upon its synthesis or extraction process. For instance, while natural MoS₂ predominantly appears in the "2 H phase", its synthetic counterpart might exhibit the 3 R (rhombohedral) phase Chhowalla et al. (2013).

Electronic and Band Structure

The richness in chemical compositions and structural variations among (TMDCs) results in various electronic properties. We discuss here the band structures of the TMDCs formed by group VI transition metals, namely Mo and W, paired with S and Se, manifesting as semiconductors in their energetically stable 2 H phase (Figure 1.5 b)). Notably, this characteristic rendered these materials potential candidates for electronic devices in two-dimensional arrangements Radisavljevic et al. (2011).

The electronic band structure of these TMDCs, especially 2 H–MoS₂, takes a remarkable evolution when transitioning from bulk to a monolayer. Calculations based on first principles, such as Density Functional Theory (DFT), depict this transformation from an indirect to a direct band gap Splendiani et al. (2010); Mak et al. (2010) (Figure 1.5 c)). At the Γ –point, the band gap transition in the bulk material is indirect but becomes direct in the monolayer Liu et al. (2012). Notably, the direct excitonic transitions at the K–point are consistent regardless of layer number. Splendiani et al. (2010). This shift is accredited to quantum confinement and a consequent change in hybridization between the p_z orbitals on the chalcogen atoms and the d orbitals on the transition metal atoms Mak et al. (2010); Splendiani et al. (2010); Wang et al. (2012). In materials like MoS₂, conduction-band states at the K–point are mainly derived from d orbitals of Mo atoms between the S layers, showing minimal interlayer interaction effects. In contrast, states at the Γ –point,

formed by combining S atom p_z -orbitals and Mo atom d orbitals, exhibit notable interlayer couplings Splendiani et al. (2010). Consequently, while direct excitonic states near the K-point remain consistent across layers, those at the Γ -point shift from indirect to direct Splendiani et al. (2010). A monolayer of $2H - MoS_2$ has a band gap of about 2.16 eV , in contrast to the 0.88 eV of its bulk form Hill et al. (2016).

A captivating feature of these monolayer TMDCs is the location of their valence band maximum and conduction band minimum at the hexagonal Brillouin zone's corners, specifically at points K and K'. Such a trait is similar to graphene and paves the way for potential valleytronics applications. Furthermore, in monolayer $2H - MoS_2$, time-reversal symmetry leads to an inverse spin splitting at the K and K' points, as schematically shown in Figure 1.5 d). This feature, known as spin-valley coupling Xiao et al. (2012), bridges valley and spin polarizations. This phenomenon is particularly pronounced in the valence band, exhibiting a range from 0.15 eV in $2H - MoS_2$ to a 0.46 eV in $2H - WSe_2$ Zhu et al. (2011) Such an interaction offers promising avenues for spintronic applications without the need for magnetic materials Pulkin and Yazyev (2016); Habe and Koshino (2015); Manzeli et al. (2017).

Synthesis

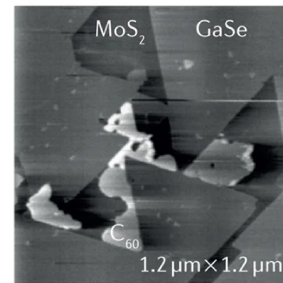
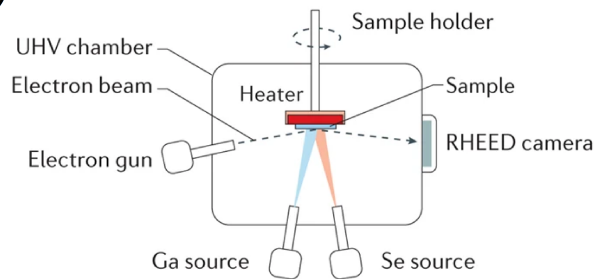
Achieving the unique and diverse properties of TMDCs requires precision in their synthesis. Over the years, a repertoire of methods has been developed to synthesize these 2D materials, each with merits and challenges. Understanding these synthesis techniques is pivotal for fine-tuning the properties of TMDCs and scaling their production.

The first high-performance transistors made of monolayers of MoS_2 were obtained from crystals of the naturally occurring mineral molybdenite Radisavljevic et al. (2011). *Chemical Vapour Transport* was primarily used for growing bulk crystals. This method relies on a transport agent, typically a halogen gas, to move the material of interest from a source region to a cooler target region Wilson and Yoffe (1969). This method has been pivotal in early studies of TMDCs such as MoS_2 , $MoSe_2$ and WS_2 crystals in the 1960s Wilson and Yoffe (1969), setting the groundwork for understanding their optical and electrical properties.

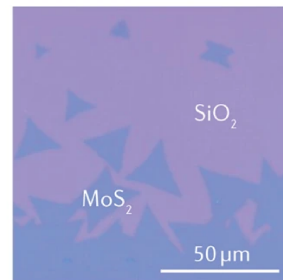
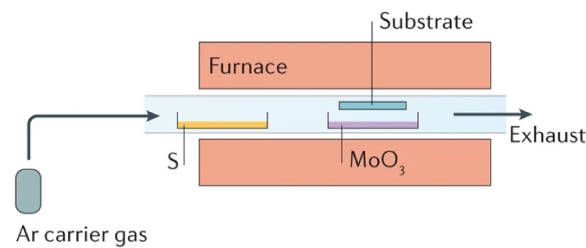
Mechanical Exfoliation: One of the initial methods employed for TMDCs synthesis was mechanical exfoliation, also known as the "Scotch-tape method" Yi and Shen (2015), leveraging the weak van der Waals interactions between layers. Here,

adhesive tape is used to exfoliate thin flakes from bulk crystals, similar to how graphene is derived from graphite Novoselov et al. (2004, 2005); Radisavljevic et al. (2011); Benameur et al. (2011). It has been crucial for rapid prototyping of devices based on TMDCs due to its simplicity and low cost. While producing high-quality samples, however, the method could be more scalable and has challenges related to limited areas of uniform material and unpredictable deposition locations that restrict its application primarily to research studies and fundamental investigations and, more so, industrial commercialization Manzeli et al. (2017).

a) Molecular beam epitaxy



b) Chemical vapour deposition



c) Metal-organic chemical vapour deposition

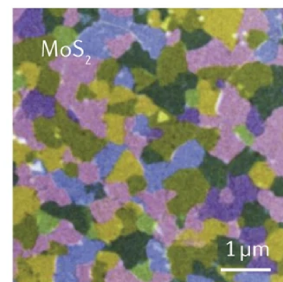
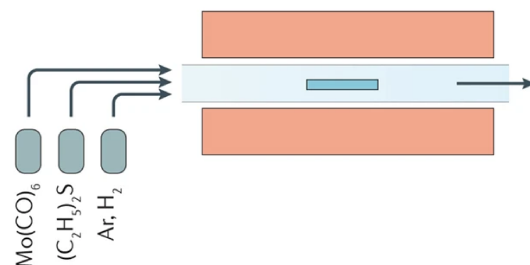


Figure 1.6 – **a)** Molecular beam epitaxy uses high-purity sources in an ultra-high vacuum. An atomic force microscopy image of GaSe on MoS₂ is shown on the right. **b)** Chemical vapor deposition involves distinct precursors. A triangular single-crystalline domains of MoS₂ on SiO₂ on the right. **c)** Metal-organic vapour deposition decomposes metal-organic precursors, showcasing a MoS₂ monolayer with varied grain orientations. Adapted from Manzeli et al. (2017).

Liquid-Phase Exfoliation: This method offers a scalable alternative to mechanical exfoliation by producing solutions containing TMDC flakes with controllable thickness Joensen et al. (1986). This process entails dispersing TMDCs in suitable solvents and then subjecting the dispersion to ultrasonication Coleman et al. (2011); Nicolosi et al. (2013); Chhowalla et al. (2013). Experiments can be traced back on Li intercalation from the 1970s Dines (1975). This method is advantageous for the bulk production of TMDC nanosheets, although the layers produced might not always be monolayers. The challenge here lies in choosing the appropriate solvent that matches the surface energy of the TMDC to prevent restacking. Despite being scalable, the method poses drawbacks such as small grain size, high defect density, potential contamination, and limited size of the flakes, which tends to overlap the flakes and present a sizeable in-plane resistance of the films Eda et al. (2011); Kang et al. (2015); Manzeli et al. (2017).

Molecular Beam Epitaxy (MBE): A more advanced technique and one of the first scalable methods, MBE allows for the epitaxial growth of TMDC layers on substrates under ultra-high vacuum conditions Manzeli et al. (2017). Detailed information on this method can be found at Joyce (1985) (Figure 1.6 a)). Precise control of the stoichiometry and layer thickness is achievable with MBE. However, it requires rigorous conditions and is a complex procedure, and the films produced often contain defects and grain boundaries affecting their electrical properties. MBE's long growth time and equipment costs are other challenges Koma et al. (1990); Chambers et al. (2001); Manzeli et al. (2017).

Chemical Vapor Deposition (CVD): CVD is a widely-used method due to its potential for scalable and high-quality monolayer production Liu et al. (2012). Volatile precursors for the transition metals and chalcogens are decomposed on substrates under controlled temperatures (Figure 1.6 b)). Initial studies on MoS₂ synthesis employed a method wherein sulfur was reacted with pre-deposited Mo on a substrate Zhan et al. (2012). Subsequent methods involved dip-coating substrates in a (NH₄)₂MoS₄ solution and then annealing them in a gas flow Liu et al. (2012), Shi et al. (2012) or by growing multilayers using MoO₃ and S as precursors Lee et al. (2012). However, these initial studies lacked precision control over the material's thickness. It was only in 2013 that reports emerged detailing the growth of monolayer MoS₂ domains on SiO₂, as highlighted in two concurrent publications Najmaei et al. (2013), van der Zande et al. (2013). Through CVD, uniform and large-area monolayers of TMDCs have been achieved Zhan et al. (2012); Liu et al. (2012); Shi

et al. (2012); Lee et al. (2012). The process is relatively cost-effective, does not require ultrahigh vacuum chambers, and allows for tunable properties based on the choice of precursors and growth conditions. However, ensuring consistent layer thickness, crystallinity across large areas and orientation remains challenging Najmaei et al. (2013); van der Zande et al. (2013); Vu et al. (2017); Lin et al. (2015).

Metal-Organic CVD (MOCVD): MOCVD is an offshoot of CVD, focusing on the use of gas-phase precursors Chung et al. (1998); Dumcenco et al. (2015); Eichfeld et al. (2015). Gaseous organic molecules, which contain transition metals (either Mo or W) and chalcogens (either S or Se), are introduced onto a substrate. They are then thermally decomposed to deposit a TMDC thin film on the substrate. MOCVD allows for precise control over the partial pressures of the precursors, ensuring uniform deposition on the large size of the substrates Chung et al. (1998); Dumcenco et al. (2015); Eichfeld et al. (2015); Kang et al. (2015). The method can produce large-area monolayers with good electrical properties. However, toxic precursors, high equipment costs, and issues related to layer control and film uniformity are challenges Kang et al. (2020).

The primary focus of reported CVD studies centers on MoS₂ growth. However, other TMDCs, including MoSe₂ Chang et al. (2014), WS₂ Kang et al. (2015), WSe₂ Eichfeld et al. (2015), ReS₂ Hafeez et al. (2016b), ReSe₂ Hafeez et al. (2016a), MoTe₂, and WTe₂ Zhou et al. (2017), have also been synthesized using CVD and MOCVD methods. Nonetheless, comprehensive characterizations of the electrical properties of these large-area films are still to be further investigated.

In essence, the synthesis of TMDCs involves a range of various methods, each one tailored to specific purity requirements, scalability, and desired properties. As research progresses, refinements and innovations in these methods continue creating new ways to incorporate TMDCs into next-generation devices efficiently.

1.5.3 Transition Metal Nitrides (TMNs)

Transition metal nitrides (TMNs) are a class of compounds formed by the insertion of electronegative nitrogen atoms into the interstitial sites of the parent metal lattice Meng et al. (2022), are characterized by covalent compounds, ionic crystals, and transition metals Zeng et al. (2022); Lu et al. (2021). One intriguing aspect of TMNs is their similarity to Group VIII noble metals like Pt and Pd, both in terms of surface and adsorption properties. This similarity arises due to the increased

atomic distance between metal atoms and the downward shift of the d-band center upon nitrogen incorporation Wu et al. (2022); Park et al. (2021); Meng et al. (2022).

Structurally, TMNs can adopt three forms, face-centered cubic (fcc), hexagon-closed packed (hcp), and simple hexagonal (hex) Gao et al. (2018). Compared to analogous oxides and sulfides, TMNs manifest enhanced covalent and metallic attributes. Their distinct electrical conductivity, robust chemical stability, enhanced mechanical attributes, high melting points, hardness, high Young's modulus, and wide band gap have positioned them as preferred materials in applications like electrocatalysis and the hydrogenation/desulfurization of fuel oil, synthesis/decomposition of ammonia among other Zhang et al. (2020); Chen et al. (2022); Xu et al. (2019); Yang et al. (2022); Xi et al. (2019); Balogun et al. (2015); Alexander and Hargreaves (2010); Chen (1996); Zhang et al. (2016); Luo et al. (2023).

TMNs have gathered significant attention in the scientific community. However, despite this growing interest, there remains a limited amount of research dedicated to their preparation strategies. The synthesis of TMNs primarily relies on two main approaches: physical and chemical methods. Physical methods include techniques such as laser ablation, sputtering (Section 2.1.1), arc discharge, and physical vapor deposition Zhu et al. (2002); Soo Kang et al. (2015); Uchida et al. (2004); Liu et al. (2016). In contrast, chemical methods consist of direct nitriding of transition metals, nitriding of metal oxides, ammonolysis of metal chlorides, solvothermal processes, and thermal decomposition of polymer precursors Weil and Kumta (2001); Shi et al. (2020); Aslanzadeh (2018); Yao et al. (2009); Meng et al. (2022).

1.5.4 Challenges in the Fabrication of Zirconium Nitride (ZrN)

Zirconium Nitride (ZrN) is a remarkable Transition Metal Nitride that is known for its exceptional hardness, resistance to corrosion, and stability when exposed to high temperatures Rizzo et al. (2012). This material's eye-catching golden hue has added elegance to jewelry and durability to aerospace components Staia et al. (2019). However, it is also prized for its critical electrical and optical characteristics that enable the development of microelectronic and optoelectronic devices Purandare et al. (2011). The face-centered cubic crystalline structure of ZrN is similar to common table salt but with superior mechanical and electronic properties, making it particularly appealing for creating tough wear-resistant coatings and for use in electronic gates Meng et al. (2022). Historically, expensive materials like tungsten (W), silver (Ag), gold (Au), and aluminum (Al) have been used in thermophoto-

voltaics (TPVs) Naik et al. (2013); Lenert et al. (2014). Still, their high cost and lower melting points limit their effectiveness at high temperatures. ZrN offers a cost-effective and accessible alternative with a superior melting point of 2980°C Domagala et al. (1956), making it ideal for TPV applications. This stability, along with its promising optical properties, positions ZrN as an excellent candidate for studying the optical characteristics of MoS_2 within the (HMMs) structures. However, producing high-quality ZrN films using Physical Vapor Deposition Magnetron Sputtering is challenging and requires careful considerations to achieve the desired behavior Signore et al. (2010); Mascaretti et al. (2021); Re et al. (2003).

The *presence of oxygen* is a significant obstacle during ZrN deposition, which leads to the formation of non-stoichiometric ZrN Signore et al. (2010). From a thermodynamic perspective, ZrO_2 is more favored than ZrN, as indicated by the standard enthalpy of formation values of $-1097.5 \Delta_f H_{\text{solid}}^0 [\text{kJ/mol}]$ for ZrO_2 and $-365.3 \Delta_f H_{\text{solid}}^0 [\text{kJ/mol}]$ for ZrN PJ Linstrom (2011). Consequently, the formation of ZrN is susceptible to the oxygen concentration PJ Linstrom (2011). The emergence of ZrN_xO_y complexes, as shown in earlier Rutherford Backscattering (RBS) measurements conducted by the research group at the Laboratory of Nanometallurgy at ETH Zürich demonstrated that an increased oxygen content can compromise the optical properties of the resultant material, reducing its metallic nature with increasing oxygen levels PJ Linstrom (2011). Consequently, employing Yttrium (Y) as an "oxygen gatherer" is crucial. Its lower standard reduction potential compared to ZrN, which means a higher oxidation potential, positions yttrium as a prime candidate to mitigate oxygen contamination during deposition.

The *substrate temperature* during deposition plays a crucial role in determining the properties and quality of the deposited films. Temperature affects atom mobility on the surface, thereby influencing diffusion processes essential for crystal growth Zhu et al. (2021). ZrN thin films with an NaCl structure predominantly exhibit either (111) (lowest strain energy) or (200) (lowest surface energy) orientations, driven by lowest strain and surface energies respectively Penttinen et al. (1988). The (200) orientation is typical of low-energy deposition, whereas (111) is more common under high-energy conditions. Notably, as film thickness increases, there is an observed shift from the (200) to the (111) orientation due to the prevailing strain energy Roman et al. (2011). Enhanced deposition temperatures significantly improve the quality of ZrN films, characterized by decreased resistance and higher purity Re et al. (2003); Rizzo et al. (2012). Optimal deposition temperature is crucial; it en-

suers atoms effectively integrate into surface lattice sites while preventing unwanted diffusion and intermixing between pre-existing layers when the temperature is too high Oura et al. (2003). Larijani et al. demonstrated that a deposition temperature of 450°C produces a ZrN film with a most pronounced metallic behaviour Larijani et al. (2011).

Substrate bias serves as another influential factor during ZrN deposition, with specific implications for oxygen contamination in the films Signore et al. (2010). The bias facilitates ion acceleration, leading to a higher ratio of atoms that can reach the film, influencing the quality of the formed films. For example, applying a DC bias can reduce the oxygen content in the films by reducing porosity, which means a denser film Re et al. (2003). Furthermore, the bias can affect the film's resistivity, reflectivity, grain orientation, higher ionization degree and improve surface mobility Re et al. (2003); Kavitha et al. (2014); Simon et al. (2016); SAOULA et al. (2019). Adjusting the bias voltage, as supported by various studies Mascaretti et al. (2021), can help achieve the desired characteristics in ZrN films.

In conclusion, while the reactive magnetron sputtering technique offers a promising route for ZrN deposition, addressing the challenges of oxygen contamination, substrate temperature, and substrate bias remains crucial to producing high-quality films tailored for specific applications.

1.6 Objective of the Study

This study addresses a critical challenge: devising a scalable and versatile method for producing (MoS₂) films. The proposed strategy is a two-step bottom-up approach using magnetron sputtering deposition. This technique is designed to synthesize MoS₂ films that are uniform and controllable in their structure, ranging from thin 2D layers to thicker, more bulk-like materials.

The primary goal is to fine-tune the deposition parameters to achieve consistent, high-quality MoS₂ films on a wafer scale. We plan to use simulations in *Mathematica* to predict the optical properties of the films and to improve the deposition process based on these insights iteratively. Additionally, we aim to explore the production of MoS₂-based hyperbolic metamaterials to leverage their unique optical characteristics for advanced optoelectronic applications.

By accomplishing these objectives, this thesis will contribute to the practical

application of MoS₂ in optoelectronic devices, offering a new perspective in materials science and potentially changing how these devices are produced.

Chapter 2

Methods

2.1 Film deposition

2.1.1 Physical vapor deposition techniques (Sputtering)

Sputtering is a physical vapor deposition (PVD) technique where atoms are ejected from a target by bombardment with highly energetic particles and then deposited to form a thin film on a substrate. Unlike other PVD methods, sputtering does not require chemical reactions to grow the film. The process involves the creation of a plasma in an inert gas environment, usually Argon (Ar), where an electric field is applied between the anode (target) and cathode (substrate) to ionize the gas. The Ar^+ ions are then accelerated towards the target and transfer their kinetic energy to the surface, ejecting atoms from the target. Some of these ejected target atoms are deposited on a substrate with the correct stoichiometry that would depend on geometry, pressure, and substrate temperature Rabe et al. (2007). A schematic of the electrode configuration in the off-axis sputtering process is shown in Figure 2.1.

When a target is made of an insulating material, the DC sputtering process described above will not work. This is because charge accumulates at the surface of the insulating target, which neutralizes the external electric field and causes the plasma to be extinguished. However, this limitation can be overcome by using an AC field at radio frequency in a process known as RF sputtering.

In RF sputtering, the insulating target acts as the "cathode," while the rest of the vacuum chamber, including the substrate, acts as the "anode" and is typically grounded. The RF field generates a plasma, but only the electrons are light enough

to respond to the AC field, while the Ar^+ ions are insensitive to it and only see the average electric field. As the substrate and the chamber constitute a very large anode concerning the target, back sputtering from the Ar^+ ions of the substrate is negligible, and the positive ions keep impacting the target for most of the deposition time.

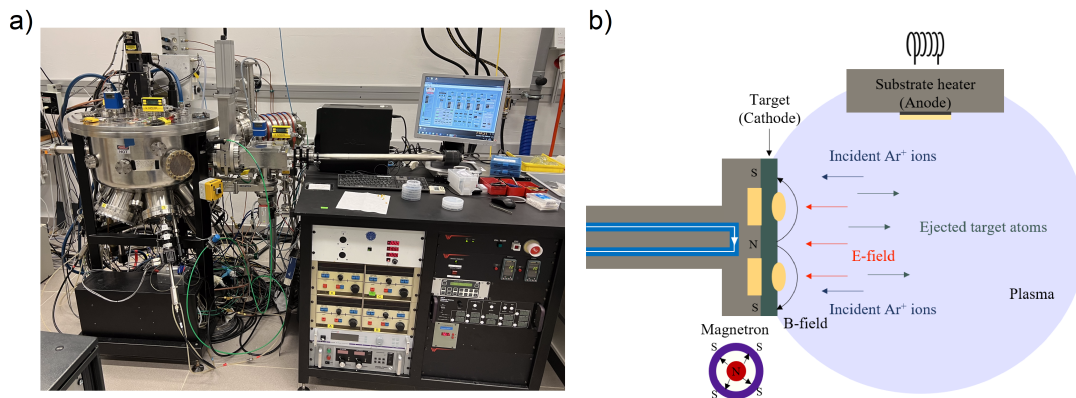


Figure 2.1 – a) Physical vapor deposition equipment (PVD Products Inc.). b) The key components of a sputtering gun highlight the ability of the magnetron to confine electrons near the surface of the target by generating a magnetic field. Additionally, the diagram shows a substrate heater in off-axis geometry, although not to scale. The image on the left is adapted from DOMINGUEZ ORDONEZ (2021).

The process of reactive magnetron sputtering (RMS) involves the co-deposition and reaction of constituents or the reaction of deposited species with the surrounding gas. Typically, argon gas is introduced into the deposition chamber as a carrier gas, along with a small amount of a second reactive gas such as nitrogen or oxygen. The reactive gas reacts with both the target surface and the sputtered metal atoms, resulting in the formation of a thin film on the substrate surface Aissani et al. (2022). This method deposits compound materials by forming a reaction between the sputtered target atoms and the reactive gas. Although RMS can be adapted for both DC and RF processes, DC is less expensive, as opposed to *RF* systems. This is because metal targets used in *DC* sputtering do not experience charging issues, making the process more cost-effective.

In this study, thin films of MoS_2 and ZrO_xN_y were deposited using a magnetron sputtering system from PVD Products Inc. Pure targets of MoS_2 (99.99% purity, MaTeck GmbH) and Zr (99.99% purity, MaTeck GmbH) were utilized, with the Zr target employed for reactive sputtering to synthesize ZrO_xN_y . The deposition chamber at the Laboratory of Nanometallurgy at ETH Zürich incorporates

all the operational principles and aspects previously discussed for sputtering deposition. These parameters were meticulously optimized to cultivate high-quality thin films. The deposition process started with the chamber pressure regulated between 6.0×10^{-7} and 1.8×10^{-6} Torr to minimize contamination. For the MoS₂ target, plasma ignition was initiated by setting the argon gas flow to 20 sccm, the chamber pressure to 15 mTorr, and the RF power supply to 25 W. The power was ramped up to 50 W over one minute and maintained for two minutes before adjusting the system to the deposition conditions (10 sccm Ar, 5 mTorr, and 75 W). Upon reaching the optimal conditions, the deposition sequence was initiated. Post-deposition, the power was gradually reduced to 25 W over two minutes before turning off the supply, and the chamber was subsequently purged with argon gas for three minutes. The films were deposited on various substrates, including microscope glass slides, Si wafers layered with 50 nm SiO₂ and Si₃N₄, and ZrO_xN_y. For the ZrO_xN_y films, the deposition parameters were set to 30 sccm Ar, 3 sccm N₂, and 3 mTorr, with a DC power of 250 W and a substrate bias of 100 V DC. The temporal protocol for pre-deposition and post-deposition conditions mirrored that used for MoS₂ depositions. Multilayered films of MoS₂ and ZrO_xN_y were fabricated sequentially, repeating the outlined procedures.

2.2 Annealing

For the thermal treatment of our samples, we employed an RTA System for the Rapid Thermal Annealing (RTA) of our wafers, capable of operating in ultra-high vacuum (UHV) conditions or controlled atmospheres such as oxygen or nitrogen. With a variable pressure range up to atmospheric pressure. The core heating mechanism includes a series of high-intensity quartz lamps, which uniformly heat the wafer. The apparatus features two primary chambers: a load-lock chamber and the process chamber. Both are maintained under UHV conditions to prevent contamination. The evacuation of these chambers is managed by turbomolecular pumps, which efficiently achieve a broad pressure measurement spectrum, from 1000 mbar down to an impressive 10^{-9} mbar. Sample transfer into the reaction chamber is facilitated by a sophisticated, magnetically coupled transfer system CreaTec (2017).

Post-deposition, the samples were subjected to an RTA process using a system provided by CreaTec Fischer & Co. GmbH. Throughout the annealing stage, the vacuum was tightly controlled, maintaining a level around 8.0×10^{-7} mbar. The annealing of amorphous MoS₂ was conducted at 485°C to induce crystallization. We

also investigated the reflectance and resistivity of MoS₂ by applying a spectrum of annealing temperatures ranging from 177°C to 627°C. The ramping process was methodically programmed to a heating rate of 5°C/min and a cooling rate of 50°C/min. However, in the lack of an active cooling system, the cooling rate was uncontrolled. Upon achieving the target temperature, we maintained the samples at this steady state for 2 hours to ensure uniform treatment. The multilayer structures combining MoS₂ and ZrN underwent annealing at 485°C, adhering to the same protocol.

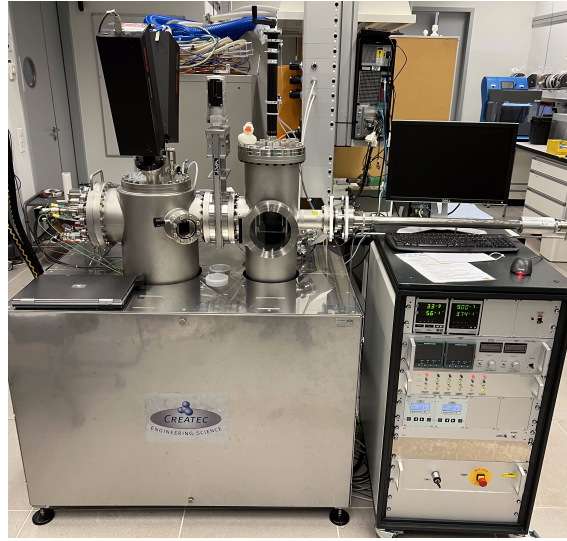


Figure 2.2 – Setup of the Rapid Thermal Annealing system used in our experiments.

2.3 Optical characterization techniques

2.3.1 Raman spectroscopy

Raman spectroscopy is a non-invasive vibrational spectroscopic technique based on the interaction of light with the vibrational states of molecules. If we consider light as a stream of particles, known as photons, several outcomes are possible when they encounter matter: absorption, scattering, reflection, or transmission without interaction.

This technique primarily observes the scattering phenomena. When using a monochromatic laser light source, photons that scatter without absorption can still transfer energy to the molecules without needing their energy to match the specific energy gap of the molecular vibrational states. A photon's collision with a molecule temporarily elevates the molecule to a virtual energy state—an unstable condition from which the molecule quickly reverts to a stable state. Typically, the molecule

returns to its initial energy level, resulting in elastically scattered photons with unchanged energy, known as *Rayleigh scattering*. In contrast, a *Raman scattering* event involves the molecule ending up in a different energy state, leading to the emission of a photon with a shifted energy, known as inelastic or Raman scattering.

Raman scattering is of two types: *Stokes* and *anti-Stokes*. *Stokes* scattering involves the molecule absorbing energy and transitioning from its ground state to a higher vibrational state, resulting in a photon with decreased energy and a longer wavelength (red-shift). *Anti-Stokes* scattering involves a molecule in an excited state transferring energy to a photon, thus moving to a lower energy state, which leads to a photon with increased energy and a shorter wavelength (blue-shift), as illustrated in Figure 2.3 Baker et al. (2016); Banwell and McCash (1994).

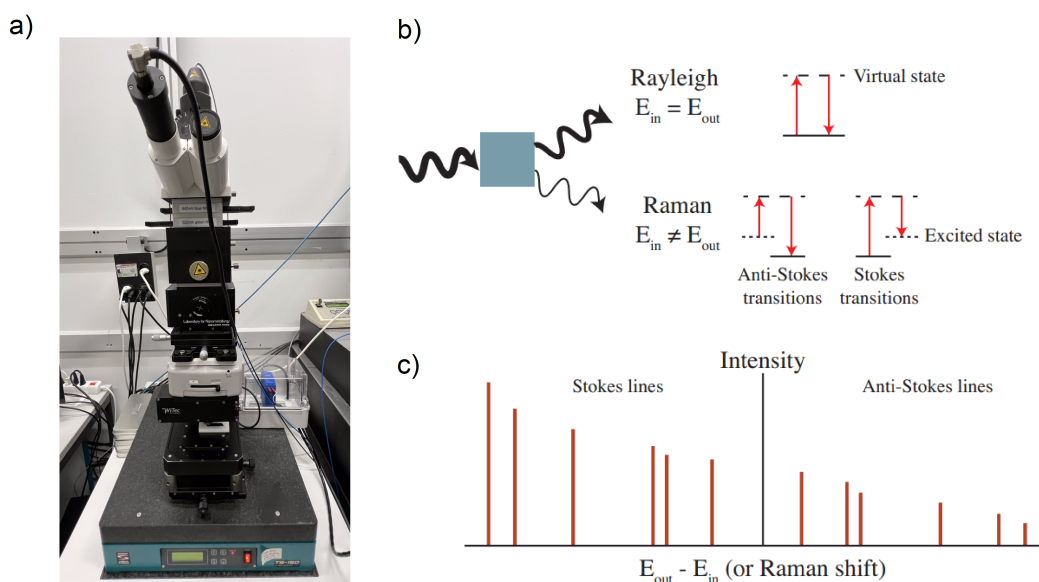


Figure 2.3 – a) the Raman setup used (Witec alpha 33 RA with a 532 nm laser) b) a simplified schematic of the difference between Rayleigh and Raman scattering and c) example of a possible Raman spectrum, omitting the powerful Rayleigh intensity at zero Raman shift and including both Stokes and anti-Stokes scattering signal. b) and c) adapted from FOWLIE (2018)

The efficiency of Raman scattering is inversely proportional to the fourth power of the laser wavelength *Scattering sensitivity* $= \lambda^{-4}$ Banwell and McCash (1994), implying that shorter-wavelength lasers produce more intense Raman signals. However, a higher laser light intensity increases the risk of sample damage.

One significant challenge in Raman spectroscopy is fluorescence, which has a longer duration between absorption and emission than the near-instantaneous Ra-

man scattering. This fluorescence can mask the Raman signal, which is inherently weak by comparison Banwell and McCash (1994).

At the core of our Raman system, we have a monochromatic green laser with a wavelength of 532 nm, chosen for its balance between sensitivity and fluorescence response, with optics arranged to focus the laser on the sample and collect the scattered light (Figure 2.3a)). The Rayleigh filter is crucial in this setup, filtering out the intense Rayleigh scattered light to allow the weaker Raman signal to be measured. The scattered light passes through a diffraction grating (2400 g mm^{-1}) that sorts the light by wavelength, providing a spectral resolution that enables us to distinguish different Raman shifts. The final detection is done by a multi-channel charge-coupled (CCD) device, which captures the diffracted light and converts it into an electrical signal, forming a Raman spectrum that plots intensity against wavenumber (w) in cm^{-1} , revealing the energy shifts characteristic of the sample's molecular vibrations. *The wavenumbers exhibit an inverse relationship with wavelength. They, therefore, are directly proportional to frequency following $w(\text{cm}^{-1}) = \frac{10^7}{\lambda}$.* The wavenumbers shown on the x -axis of a Raman spectrum are indicative of the Raman shift, which is the variance between the original laser frequency (λ_1) and the frequency change caused by the Raman effect (λ_2), as illustrated in $\Delta\lambda = \lambda_1 - \lambda_2$. This Raman shift can be further converted into a wavenumber shift (Δ) by $\Delta w = \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \cdot 10^7$. This shift is directly related to the energy levels involved in the molecular vibrations and rotations probed by the Raman spectroscopy. The wavenumber shift provides a spectral "fingerprint" that can be used to identify specific molecular bonds and structures Banwell and McCash (1994).

To investigate the Raman active modes of molybdenum disulfide (MoS_2), Raman spectroscopy was employed both pre- and post-annealing. A distinct difference in the Raman signatures between crystalline (x- MoS_2) and amorphous (a- MoS_2) forms was expected due to the distinct long-range translational symmetry inherent to crystalline materials. This symmetry allows incident photons to excite phonons, leading to sharp Raman peaks. Conversely, the lack of such order in amorphous structures typically results in broader peaks Tuschel (2017). To address the fluorescence challenges presented by the highly reflective ZrO_xN_y substrate, we employed Si_xN_y wafers as an alternative for MoS_2 deposition, enabling more accurate Raman spectroscopic observations. For the measurements, we used a Raman spectroscopy Witec alpha 33 RA with a 532 nm green laser for the excitation.

2.3.2 Ellipsometry

Ellipsometry is a non-destructive optical technique that measures the change in polarization of light upon reflection or transmission through a sample. It is well-known for its sensitivity and precision in characterizing material properties, such as optical constants (n , k , or ϵ_1 , ϵ_2), film thicknesses, doping concentrations, and surface or interface roughness J.A. Woollam Company (2008). The principle of ellipsometry can be represented mathematically (see Equation 1.6), where it quantifies the complex reflectance ratio of the p-polarized (rP) to s-polarized (rS) light components. Since this ratio is a complex number, the measurement intrinsically includes phase information (Δ), greatly enhancing sensitivity and reproducibility J.A. Woollam Company (2008).

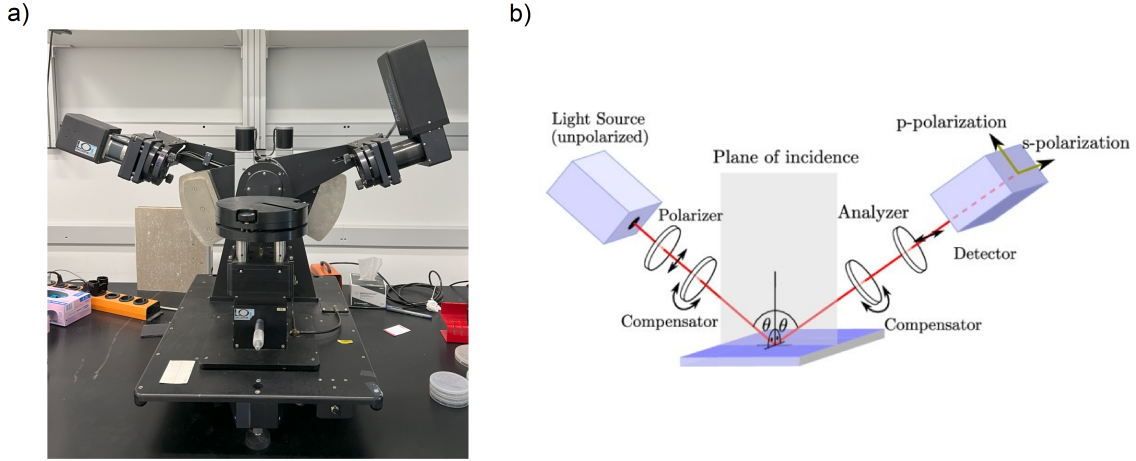


Figure 2.4 – a) J.A. Woollam Co. Variable Angle Spectroscopic Ellipsometer (VASE). b) Schematic of an ellipsometer setup. The image on the right is adapted from Negara (2016).

For the precise characterization of thin films, we utilized a J · A · Woollam M–2000 ellipsometer (Figure 2.4), measuring the amplitude Ψ and the phase shift Δ . Data were collected at multiple angles of incidence– 55° , 60° , and 65° –across a wavelength spectrum of 250–950 nm. The Wvase32 software was employed for fitting the ellipsometric data. Ellipsometry data analysis necessitates constructing an optical model that can accurately reproduce the experimentally measured Ψ and Δ values to extract valuable properties of a sample, such as film thickness and optical constants. The optical model comprises the substrate’s optical constants and the thickness and optical constants of each layer within the sample stack. Our multilayer sample stack, which includes layers of Si–SiO₂–Si₃N₄–ZrO_xN_y, necessitated a complex optical model. Reference constants for Si and SiO₂ were obtained from REFERENCE

J.A. Woollam Company (2014), and for Si_3N_4 , from REFERENCE Palik (1998). The a-MoS₂ and x-MoS₂ layers were modeled using data from REFERENCE Jellison (1992) and the Wvase32 software's material library, such as Gallium Arsenide (a-GaAs) which is a good candidate because it is also a semiconductor. The ZrO_xN_y parameters were derived from metallic-like structure files available at the Laboratory of Nanometallurgy at ETH Zürich. The software analysis allowed for certain fixed parameters while optimizing others to achieve the best fit, minimizing the mean squared error (MSE) Tompkins and Irene (2005).

Reflectance measurements of p and s polarized light, as well as their ratios for the multilayer structures, were also conducted with the ellipsometer. These measurements, especially when integrated into our simulations (Section 2.5), provided a deeper understanding of the phase characteristics within the multilayer composition. For accurate reference measurements, a baseline was established at a direct incidence angle of 90° without a sample in the light emission and collection path.

2.3.3 Reflectance

To determine the reflectance of our samples when light is at normal incidence to their surfaces, we utilized an integrated optical setup that included a UV–VIS–NIR light source (Ocean Optics DH-2000-BAL) and a high-resolution spectrometer (Ocean Optics USB 2000+). Light from the source was projected onto the samples, and the reflected light was channeled to the spectrometer for analysis. This was accomplished using a specialized reflection probe (Ocean Optics QR230-7-XSR), with a fiber core size of $230\,\mu\text{m}$ and a numerical aperture of 0.22, ensuring high resistance to solarization effects. For accurate reflectance measurement, a UV-enhanced aluminum mirror (ThorLabs PF10-03-F01) served as the standard reference.

2.4 Electrical characterization

2.4.1 Four point-probe measurement

The "four-point probe" has proven to be a convenient tool for measuring resistivities. The basic model for all these measurements is indicated in Figure 2.5. Four sharp probes are placed on a flat surface of the material to be measured. Current is passed through the outer two electrodes, while the floating potential is measured across the inner pair. For optimal results, it is essential to prevent minority carrier injection and ensure good contact by mechanically lapping the surface on which the probes

rest. For a description of the method, see Valdes (1954), which gives the functional relationship between the resistivity ρ and the voltage and current readings for various geometries.

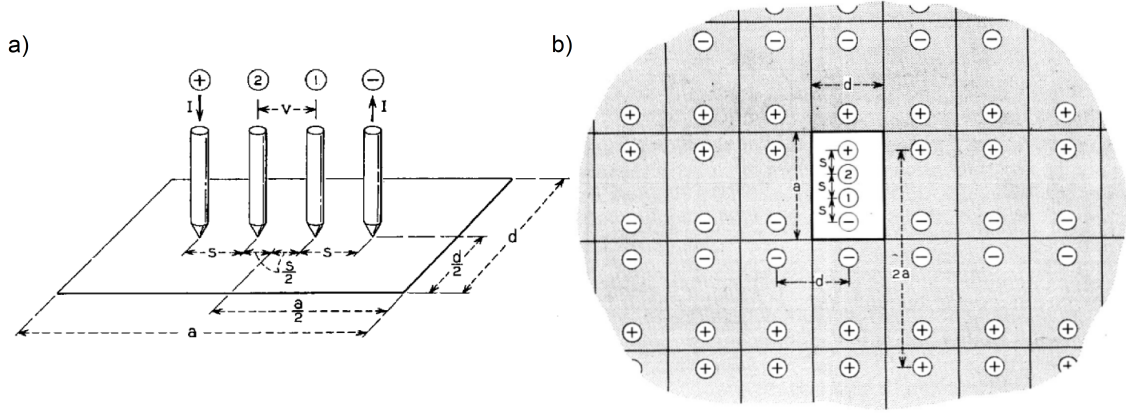


Figure 2.5 – a) Arrangement of a four-point probe on a rectangular sample b) System of images. Adapted from Smits (1958)

Method

We would develop the following mathematical construction following the work presented by Smits (1958), Valdes (1954) and Uhler Jr. (1955).

We would start by defining a current source in an *infinite sheet* that gives rise to the logarithmic potential as:

$$-\psi_0 = -\frac{I\rho_s}{2\pi} \ln r, \quad (2.1)$$

Where ψ is the potential, I the current, ρ_s the sheet resistivity (also known as surface resistance or surface resistivity), and r the distance from the current source.

In particular, the potential for a dipole (+ source and – source) becomes:

$$\psi - \psi_0 = \frac{I\rho_s}{2\pi} \ln \frac{r_1}{r_2}, \quad (2.2)$$

When using a four-point probe on a sheet, the two outer points act as a dipole for current flow. As a result, the potential difference between the two inner points is determined for an infinite sheet:

$$\Delta\psi = V = \frac{I\rho_s}{\pi} \ln 2, \quad (2.3)$$

We are going to assume that the point spacing is equal, then we can determine the sheet resistivity using the following formula:

$$\rho_s = \frac{V}{I} \frac{\pi}{\ln 2} = \frac{V}{I} 4.5324..., \quad (2.4)$$

To determine the sheet resistivity of a *finite sample*, the method of images is used.

Rectangular sample

We consider a four-point probe on a rectangular sample with the dimensions a and d . The probe is positioned symmetrically with a point spacing s , as illustrated in figure 2.5 **a**). To measure the voltage between the two center points (1 and 2), an infinite arrangement of dipoles must be taken into account, as shown in figure 2.5 **b**). These dipoles contribute to the voltage measured between points 1 and 2. With a coordinate system where the x -axis goes along the $+$ source, and the distance between these sources is d , the potential is:

$$\psi - \psi_0 = -\frac{I\rho_s}{2\pi} \ln 2 \sqrt{\sin^2 \frac{\pi}{d} x + \sinh^2 \frac{\pi}{d} y}, \quad (2.5)$$

Using this expression, we can simplify the current sources into a series of lines with alternating signs in a single direction. In the coordinate system, each line of sources is positioned such that points 1 and 2 have an x -coordinate of zero. Therefore, the original expression can be reduced to:

$$\psi - \psi_0 = -\frac{I\rho_s}{2\pi} \ln(e^{\pi y/d} - e^{-\pi y/d}), \quad (2.6)$$

The voltage V is influenced by the contribution of each line of sources. Specifically, each line of sources adds a certain amount to the overall voltage.

$$\psi - \psi_0 = -\frac{I\rho_s}{2\pi} \ln \left(\frac{e^{\pi(y_n+s)/d} - e^{-\pi(y_n+s)/d}}{e^{\pi y_n/d} - e^{-\pi y_n/d}} \right), \quad (2.7)$$

where y_n is the distance from point 1 to the center source in line n . The dimension a is involved in the values y_n . The total voltage between the points 1 and 2 is therefore

$$V = \sum \Delta\psi_n \equiv \rho_s I \frac{1}{C\left(\frac{a}{d}; \frac{d}{s}\right)} \quad (2.8)$$

Where $C\left(\frac{a}{d}; \frac{d}{s}\right)$ is a constant defined by this equation. Smits (1958) demonstrated in the Appendix of his work that expanding the logarithm and summing each term as a geometrical series can simplify the summation process. In the majority of cases, the first term of the series provides a four-place accurate result. As a result of this method, we can obtain the *sheet resistivity* by utilizing the following equation:

$$\rho_s = \frac{V}{I} C\left(\frac{a}{d}; \frac{d}{s}\right) \quad (2.9)$$

There are different correction factors reported in the literature (Smits (1958), Valdes (1954), Uhler Jr. (1955)) depending on the geometry (rectangular, narrow, circular) of the desired structure.

Measurement of body resistivities of thin samples

When using a four-point probe on a slice of finite thickness w , voltage gradients perpendicular to the surface are introduced. However, if these gradients can be considered negligible, the slice can be treated as an infinitely thin slice, allowing for the proper sheet resistivity. This, in turn, enables the determination of the body resistivity ρ , which is related to the sheet resistivity by the equation $\rho = \rho_s w$.

The resistivity of an *infinite slice* with a finite thickness w can be expressed as:

$$\rho = \rho_s w = \frac{V}{I} w \frac{\pi}{\ln 2} F\left(\frac{w}{s}\right) \quad (2.10)$$

The correction factor $F\left(\frac{w}{s}\right)$ approaches unity as w approaches zero. From Uhler Jr. (1955) paper $F\left(\frac{w}{s}\right)$ can be obtained; and it is tabulated in Table III on Smits (1958) paper. The table assesses the error that may occur when treating thin samples as infinitesimal sheets. For a finite slice of infinite thickness, the following

relation holds:

$$\rho = \rho_s w = \frac{V}{I} C \left(\frac{a}{d}; \frac{d}{s} \right) F \left(\frac{w}{s} \right) w \quad (2.11)$$

The resistance was measured using a linear four-point probe head and a Keysight B2962A power supply.

2.5 Design and Mathematica simulations

In our study, we utilized *Wolfram Mathematica* codes based on Transfer Matrix Approach (Section 1.4.2) and Effective Medium Theory (Section 1.3) to fine-tune the structural parameters of our materials to optimize its optical properties. The TMA code individually modeled each layer of the unit cell to analyze its transmission and propagation characteristics. In contrast, the EMT code considered the unit cell as a whole, treating it as an effective medium.

Optical constants n and k , determined through ellipsometry (Section 2.3.2), were incorporated into both codes. These constants were crucial for defining the optical behavior of our materials and calculating effective permittivity for both parallel and perpendicular orientations of the layers, as shown in Equations 1.13 and 1.15. We applied Fresnel's equations (Section 1.5) to establish transfer matrix operators, leading to detailed matrices for transmission and propagation in our multi-layered design.

Our optimization also considered the thickness of the structure's layers and the filling fraction of metal in the unit cells, utilizing methodologies aligned with those developed at ETH Zurich's Nanometallurgy Laboratory. We constructed an optical phase diagram using EMT to explore the material's effective behavior; we aimed to identify an Optical Topological Transition (OTT), which could range from metallic to dielectric or represent one of two types of hyperbolic metamaterials 1.4.4. The insights obtained from these models were instrumental in crafting the design of our final structures.

2.6 Additional Characterization Techniques

2.6.1 Rutherford Backscattering Spectrometry (RBS)

Rutherford backscattering spectrometry (RBS) is an ion scattering technique utilized for analyzing the composition of thin films. One of the key advantages of RBS is that it allows for quantification without the need for reference standards. During an RBS analysis, high-energy helium ions (He_2^+) are directed onto the sample, and the yield and energy distribution of the backscattered He_2^+ ions at a specific angle are measured. Using the known backscattering cross-section for each element, it is possible to generate a quantitative compositional depth profile from the obtained RBS spectrum Chirayil et al. (2017).

The RBS measurements that complement this work were carried out with the expertise of the ETH Zürich Ion Beam Physics group, a leading group in developing new instrumentation for Accelerator Mass Spectrometry (AMS) and Ion Beam Analyses (IBA).

2.6.2 X-Ray Diffraction

X-ray diffraction (XRD) analysis provides detailed insights into the crystalline structure of our materials. Using X-rays with wavelengths comparable to atomic distances, XRD can effectively determine the periodic structural arrangement of atoms and molecules. Unlike other techniques, XRD is non-destructive, allowing samples to remain intact even after analysis. To obtain a diffraction pattern, the intensity of the scattered waves is measured as a function of the scattering angle, which is the angle between the incident beam and each scattered beam following Bragg's law (Figure 2.6 a)). The peaks in an X-ray diffraction pattern correspond directly to atomic distances. When an incident X-ray beam interacts with periodically arranged atoms, a set of lattice planes with an interplanar distance of d satisfies the diffraction condition McMorrow and Als-Nielsen (2011). Bragg's law is then defined as:

$$n\lambda = 2d\sin\theta \quad (2.12)$$

where λ is the incident beam wavelength, θ is the scattering angle and n is an integer number of wavelengths λ . The Bragg condition, which can be satisfied only for wavelength $\lambda \leq 2d$.

An X-ray diffractometer consists of an X-ray source, a sample stage, and a detector. The X-ray source produces an X-ray beam with a specific energy level corresponding to the emission line of a metal, such as Cu, Al, Mo, Mg (in our case, Cu). A monochromator is used further to collimate the beam to an ideally single wavelength. The beam is then directed onto a sample stage, consisting of a plate on which the sample is mounted. The diffracted beam is collected by the detector, which can be rotated about the source position by means of a goniometer. The diffraction geometry is defined by the incident and diffracted beam angles, which are named ω and 2θ , respectively (Figure 2.6 b)). Note that in such notation, the incident ω corresponds to the angle θ of Bragg's law.

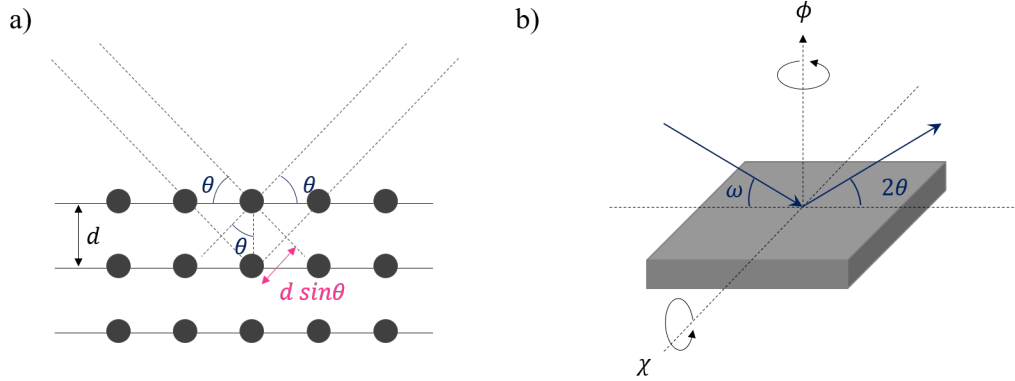


Figure 2.6 – a) The Bragg diffraction of a solid crystal. b) The description of the ω , 2θ , ϕ , χ angles of the diffractometer. Images adapted from DOMINGUEZ ORDONEZ (2021)

The X-ray diffraction measurements that complement this work were carried out with the expertise of José Luis Ocaña Pujol on a high-resolution Philips X'Pert PANalytical Material Research diffractometer. The source is an X-ray tube with a copper anode with a two bounce Ge (220) monochromator crystal that provides $\text{CuK}_{\alpha 1}$ radiation, corresponding to $\lambda = 1.5406 \text{ \AA}$.

Chapter 3

Results and discussion

3.1 Raman spectroscopy

This section presents our Raman scattering analysis for ultra-thin, few-layer, and bulk MoS₂ samples, aligning our results with the literature. Our study confirms the presence of the in-plane (E_{2g}^1) and out-of-plane (A_{1g}) Raman modes across our thickness regime. We observe a clear correlation between these vibrational modes and the layer thickness of the samples, providing a reliable method for estimating our MoS₂ samples thickness. Notably, the observed frequency shifts cannot be solely attributed to weak van der Waals (VdW) interlayer interactions, suggesting the presence of additional factors influencing the behavior.

The results shown in this section were measured in samples of MoS₂ on top of

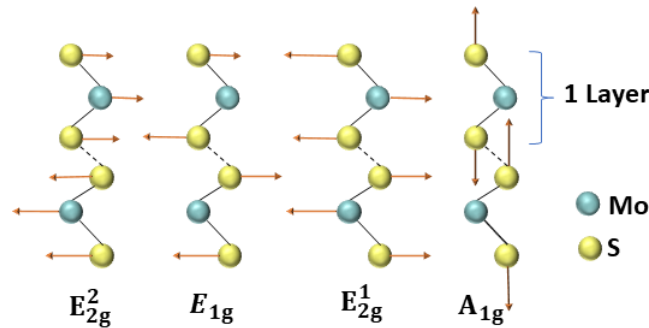


Figure 3.1 – The atomic displacements of the four Raman-active modes within the unit cell of bulk MoS₂ crystal, as observed along the $[1000]$ direction. Adapted from "Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂" by H. Lee et al., Physical Review B, 2010 Lee et al. (2010).

a 100 nm $\text{Si}_x\text{N}_y/\text{SiO}_2$. The MoS_2 on these samples was deposited at the same time as the samples on ZrN that would be brought to this discussion in the following section. This simultaneous deposition ensures uniform material thickness across different substrates, thereby maintaining consistency in the experimental conditions for the comparative analysis in our investigation.

The figures in this section 3.2, 3.3, 3.4 illustrate representative Raman spectra obtained from ultra-thin (15 s, 30 s deposition time), few-layers (1 min, 2.5 min), and bulk (deposition time greater than 2.5 min) MoS_2 samples compared with the results found at Lee et al. (2010), the first report of Raman scattering studies of single- and few-layer MoS_2 samples. Within the four Raman-active modes observed in the bulk MoS_2 crystal (Figure 3.1) Verble and Wieting (1970), we detected the E_{2g}^1 and A_{1g} modes around 400 cm^{-1} (Figure 3.2). However, the other two modes (E_{1g} , E_{2g}^2) were not detected due to either selection rules in our scattering geometry (E_{1g}) Verble and Wieting (1970) or limited rejection of the Rayleigh scattered radiation (E_{2g}^2) Verble et al. (1972) or even argue that the frequency of these two modes is too low. The E_{2g}^2 mode originates from the vibration of an S–Mo–S layer with adjacent layers. Conversely, the E_{1g} mode is prohibited in backscattering experiments on a basal plane. The in-plane E_{2g}^1 mode occurs due to the opposite vibration of two S atoms relative to the Mo atom, while the A_{1g} mode corresponds to the out-of-plane vibration of only S atoms in opposite directions Bertrand (1991). It is worth noting that ultra-thin MoS_2 exhibits a prominent in-plane vibrational mode at around 385 cm^{-1} , which corresponds to the E_{2g}^1 mode, of the bulk MoS_2 crystal (Figure 3.3) showing as Lee et al did with exfoliated single layers of MoS_2 that they retain the trigonal prismatic coordination found in the bulk material Lee et al. (2010).

In Figure 3.2, the Raman spectra exhibit robust signals from both the in-plane E_{2g}^1 and out-of-plane A_{1g} vibrations for all film thicknesses. The behavior as a function of film thickness reveals several exciting characteristics. Notably, as shown in Figure 3.2, 3.3 and 3.4 the E_{2g}^1 vibration softens (redshifts) while the A_{1g} vibration experiences stiffening (blue shifts) as the sample thickness increases, which is particularly striking. Upon reaching a film deposition time of 2.5 min, the frequencies of both modes converge to the values observed in bulk (deposition time greater than 2.5 min).

In Figure 3.3, 3.4 the relationship between the deposition time and the frequencies of these two Raman modes highlights the frequency difference $\Delta\omega$ as an exceptionally reliable "thickness indicator." By comparing these findings with the

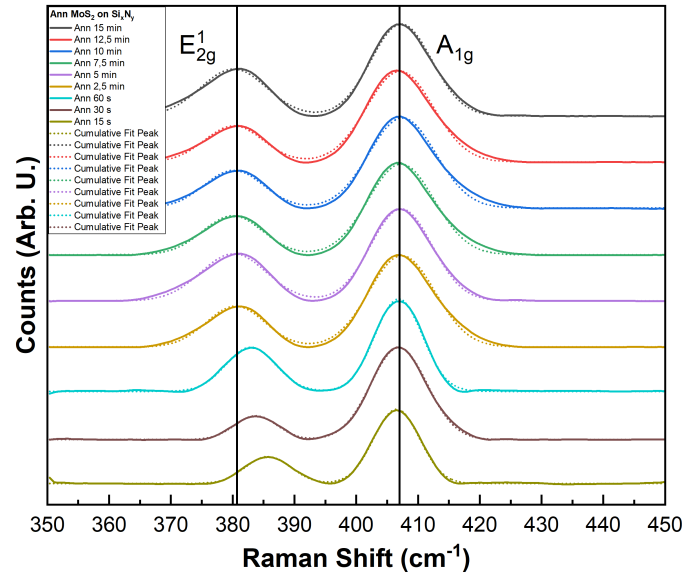


Figure 3.2 – Raman spectra of ultra-thin, few layers and bulk MoS₂ samples on Si_xN_y/SiO₂.

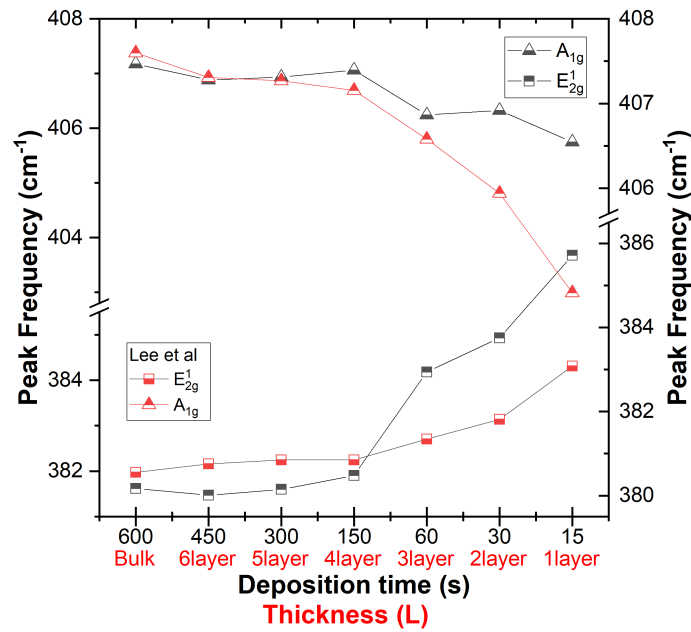


Figure 3.3 – Frequencies of E_{2g}¹ and A_{1g} Raman modes as a function of layer thickness

results presented in Lee et al. (2010), we can obtain valuable insights into the number of layers based on our deposition time. In contrast to the findings reported in Lee et al. (2010), we observed a reversed trend in our study. Specifically, the rate of frequency change was found to be twice as large for the E_{2g}^1 mode compared to the A_{1g} mode (Figure 3.3), which in the case of Lee et al was the A_{1g} mode twice as large to the E_{2g}^1 mode. Nevertheless, the observed discrepancy does not currently impact the frequency difference $\Delta\omega$ of the modes shown in Figure 3.4. We plan to address this point later, as Rutherford Backscattering (Section 2.6.1) may explain this behavior (Section 3.1).

According to Lee et al., in the case of single MoS_2 layers, the value of $\Delta\omega$ is observed to be 3 cm^{-1} smaller compared to bilayers Lee et al. (2010). Notably, this change is several times greater than the usual variation of $\Delta\omega$ observed within or between different single-layer samples, as shown in Figure 3.4. By comparing this trend with our findings, specifically the black markers at 15 s, we can confidently assert that we have fewer than three layers. Above two-and-a-half-minute deposition time, we transition into the bulk phase of MoS_2 , as the observed behavior becomes remarkably consistent. In contrast, before reaching this timeframe, we reside within the regime characterized by ultra-thin and few layers of MoS_2 . This outcome is particularly remarkable considering the deposition technique employed (section 2.1.1).

The vibrational dynamics of van der Waals layered materials are often studied by examining the transition from individual two-dimensional layers to bulk structures Verble and Wieting (1970); Bromley (1971). Classical coupled harmonic oscillator models predict a stiffening in the E_{2g}^1 and A_{1g} modes due to enhanced interlayer van der Waals interactions in the bulk Li and Galli (2007). While the A_{1g} mode's observed shift aligns with this, the E_{2g}^1 mode does not, suggesting more complex interlayer forces at play Wieting and Verble (1972). Studies on MoS_2 surfaces demonstrate a contraction in interlayer spacing and a lateral lattice expansion in single layers, implying surface reconstruction effects on intralayer bonding and lattice dynamics Bertrand (1991); Yang et al. (1991); Mrstik et al. (1977). These findings support the notion that even weak interlayer interactions can influence the bonding and lattice properties in both ultra-thin and bulk MoS_2 samples Lee et al. (2010). The anomalous trend in the E_{2g}^1 mode wavenumber $w(\text{cm}^{-1})$ with increasing MoS_2 thickness can be linked to the weakening of long-range Coulombic interactions among Mo atoms. As the layers accumulate, the dielectric tensor dampens these

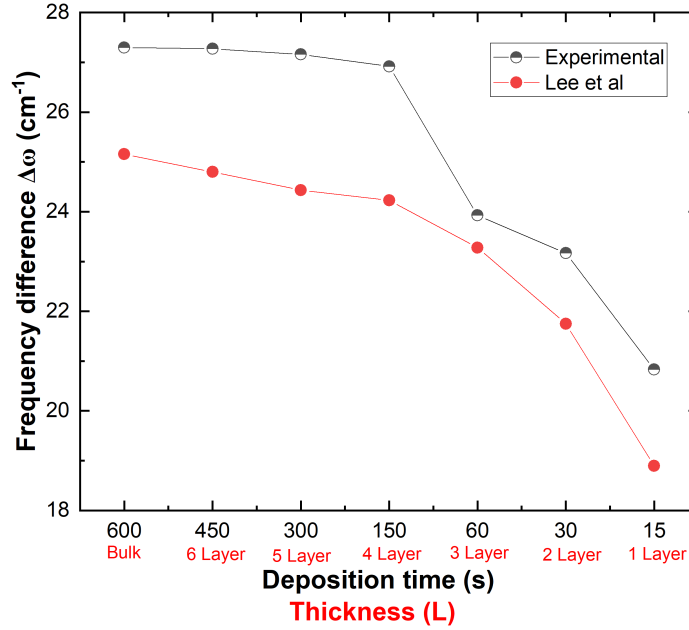


Figure 3.4 – Frequencies differences of E_{2g}^1 and A_{1g} Raman modes as a function of layer thickness

interactions, leading to the observed redshift or softening of the E_{2g}^1 mode that involves in-plane Mo atomic vibrations. In contrast, the A_{1g} mode, governed by the out-of-plane displacements of S atoms, is less affected by this dielectric screening. Instead, its wavenumber escalation is due to increased restoring forces from interlayer interactions, independent of the screening effect, which means that nearby charges diminish or "screen" the electric field's effective range and strength created by the original charge Molina-Sánchez and Wirtz (2011); Bertrand (1991); Chakraborty et al. (2013).

Rutherford Backscattering Spectrometry (RBS)

Rutherford backscattering (RBS) (Section 2.6.1) is a technique employed in this work to determine both the thickness and stoichiometry of the samples. In Figure 3.5 **b)**, **c)**, the peak positions identify the respective elements and their locations within the layer geometry. Meanwhile, the peak areas indicate the relative abundance of these elements. Notably, the spectra for the 1 min sample display traces of Argon (Ar) impurities, likely originating from the utilization of Ar in the magnetron sputtering deposition process.

Figure 3.5 **a)** depicts the derived ratio between sulfur and molybdenum con-

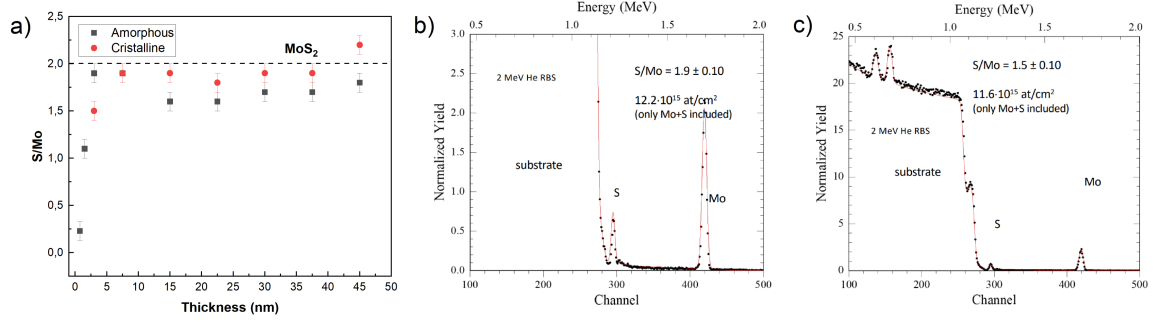


Figure 3.5 – **a)** Ratio between the Sulfur (S) and Molybdenum (Mo) content of the different samples as a function of thickness, as measured by Rutherford Backscattering Spectroscopy. Black points correspond to as-deposited samples, while red points correspond to some annealed samples. RBS of the MoS₂ on top of Si_xN_y sample for a 1 min deposition (3 nm thickness) **b)** before annealing and **c)** after annealing. The black dots are the experimental data, while the red indicates the ones annealed. The horizontal line indicates the fit from which the parameters were extracted.

tent in samples of varying thicknesses as determined by RBS. We noted that our deposition method occasionally results in slightly substoichiometric Mo/S ratios, consistent with existing literature on magnetron sputtering of MoS₂ Sirota et al. (2019); Babuska et al. (2022); Alev and Goldenberg (2023). This is particularly evident in our thinnest samples (15 s, 30 s deposition times) as we near the single (≈ 0.65 nm) and bilayer (≈ 1.3 nm) regimes Radisavljevic et al. (2011). Similarly to other studies, Figure 3.5 **a)** indicates Kim et al. (2018); Donarelli et al. (2013) that annealing in UHV causes some sulfur loss. However, while a substoichiometric Mo/S ratio is known to increase the frequency difference between the two Raman modes Alev and Goldenberg (2023); Kim et al. (2018); Donarelli et al. (2013); Parkin et al. (2016), we still observed a diminishing frequency difference as film thickness decreased, as demonstrated in Figure 3.4. This frequency variance has been identified to fluctuate based on the thickness of crystalline MoS₂ in the one-to-a few-layer regime Lee et al. (2010); Tao et al. (2015); Mazaheri et al. (2020). Getting back to the contrasting trend reported in our Raman spectroscopy results (Section 3.1) compared to that of Lee et al., where the A_{1g} mode exhibited a frequency change double that of the E_{2g}¹ mode Lee et al. (2010), we propose a potential explanation. The A_{1g} mode, is governed by the out-of-plane vibrations of sulfur (S) atoms in the MoS₂ layers. This mode's frequency is expected to increase due to stronger restoring forces from interactions between interlayer interactions. However, sulfur vacancies created during post-deposition annealing could mitigate this increase, leading to the attenuated frequency shifts we observe (Figure 3.3).

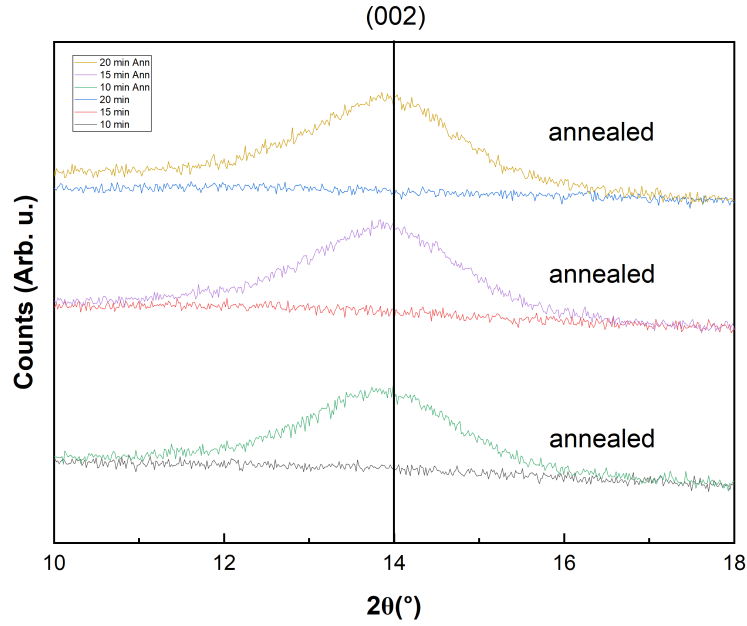


Figure 3.6 – X-ray diffraction pattern of the samples with 10 min, 15 min, 20 min of MoS₂ on a Si₃N₄ both before and after annealing. The line indicates the MoS₂ [002] peak Hassel (1924); Buck (1986); Youn et al. (2014)

X-Ray Diffraction

Figure 3.6 displays the distinctive [002] peak, which is notably present only in annealed samples. Using Raman spectroscopy, we confirmed that our as-deposited films are amorphous when deposited and only crystallize upon annealing. Here, we have an alternative technique that proves that statement through different thickness regimes (10 min, 15 min, and 20 min deposition time). Where the width of the peak indicates that our samples are polycrystalline.

Despite the polycrystalline and substoichiometry of our samples, we observe the same thickness dependance trends of MoS₂ fabricated through other methods.

3.2 Ellipsometry and Reflectance

3.2.1 Analysis of the Complex Refractive Index of MoS₂

As the complex refractive index is the most fundamental material property that describes the light-matter interaction in these 2D MoS₂ layers, several previous reports have shed light on the complex refractive index (or the complex dielectric function since one can be calculated from the other) of monolayer, few-layer and thin films of

MoS₂ Li et al. (2014); Yu et al. (2015); Hsu et al. (2019); Song et al. (2019); Islam et al. (2021).

As mentioned in the fabrication process described in section 2.1, RF magnetron sputtering is used to deposit amorphous a-MoS₂ on top of the substrate of choice. Annealing in ultra-high vacuum (UHV) (Section 2.2) can be used to crystallize MoS₂ in a subsequent step. We coated the substrate ZrN–Si₃N₄–SiO₂–Si with different deposition times for MoS₂ of 15 s, 30 s, 60 s, 2.5 min, 5 min, 7.5 min, 10 min, 12.5 min, 15 min that according to our Raman spectroscopy findings (Section 3.1) our deposition rate was of ≈ 3 nm per minute.

The optical constants of the substrate, Si₃N₄–SiO₂–Si are not expected to change noticeably after the film deposition of MoS₂ and thermal annealing processing. This was confirmed by Islam et al. by measuring an identical substrate of thermal SiO₂ on Si before and after thermal processing but with no film deposition, and so it was confirmed with previous studies done at LNM (ETH Zürich). The goodness of fit, SiO₂ thickness, and optical model were identical before and after heating, as shown in Figure S5, Supporting Information of Islam et al. (2021).

As shown in Section 1.5.3 the refractory metal ZrN has a melting point of 2980 °C. Previous work done at LNM has shown that among different substrates such as Silver Ag, Aluminum Al, Gold Au, Zirconium Nitrate (ZrN) has proved to be an excellent substrate since its optical properties and stoichiometry do not change when it is deposited nor when it is annealed along with the MoS₂, then the changes of the MoS₂–ZrN can be attributed solely to MoS₂.

The data analysis in our study involved simultaneous fitting of the measured angles and wavelengths (Section 2.3.2). Figure 3.7 presents the experimental Ψ and Δ data as solid curves, alongside the model-fitted data as dotted curves, obtained through data analysis for the 15 s deposition time of a MoS₂ sample and the substrates discussed in Section 2.3.2, where we could find good agreement between the experimental measurements and the model constructed to model and obtain the complex refractive index. Notably, an asymmetric interference-like peak at approximately 600 nm arises due to the enhancement of interference in SiO₂, resulting from the splitting of the incident beam into ordinary and extraordinary beams. This phenomenon indicates a significant anisotropy in MoS₂ Islam et al. (2021).

In general, determining the complex refractive index for thicker films tends to be more accurate due to the longer path length within the film. In this study, we

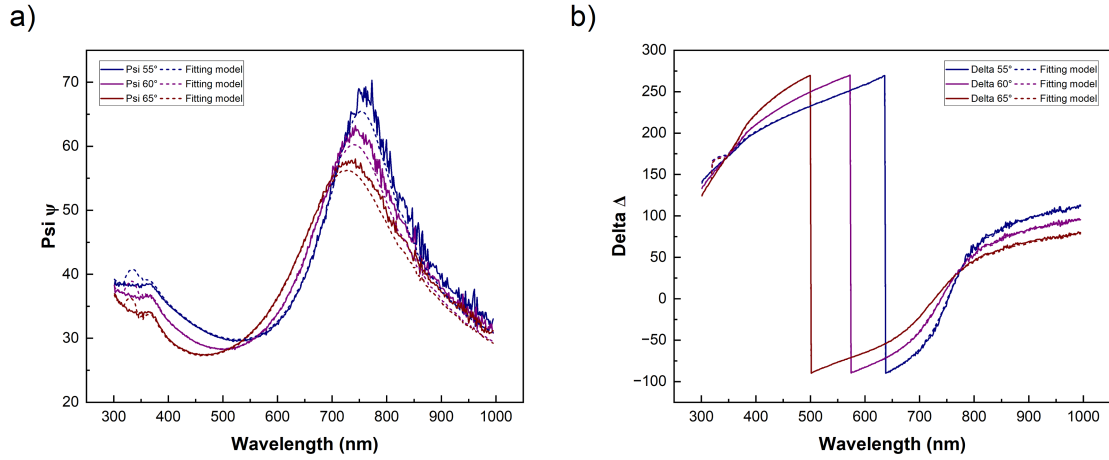


Figure 3.7 – Measured and modeled a) Ψ and b) Δ spectra of 15 s deposition time of MoS_2 versus wavelength. The solid colored lines are measured data at various angles of incidence, and the dashed lines are modeled fit values with good agreement obtained over the full spectral range.

initially analyzed the thickest "thin-film" (5 min deposition time) MoS_2 samples to determine its film thickness and optical properties and then attempted to apply these optical constants to the few-layer (1 min and 2.5 min deposition time) and ultra-thin (15 s and 30 s deposition time) MoS_2 films by keeping the optical constants fixed from the thicker film and fitting only the film thickness. It was found that the ultra-thin and few-layer samples did not analyze well using optical constants from the thickest sample, demonstrating the sensitivity of the optical constants to film thickness, which goes according to the predictions made of the tunability of the MoS_2 optical properties with thickness. Consequently, we adapted our approach: each sample was individually characterized, with the Raman spectroscopy-derived thickness as a benchmark (Section 3.1). Specifically, we applied a consistent thickness of 3 nm, correlating to a deposition time of 1 minute, as a standard for all samples. Instead of generalizing the optical constants across all thicknesses, we matched each sample with the closest deposition time's measured optical properties. This method allowed us to have a more precise correlation between the experimental measured ψ and Δ and the model constructed to obtain the complex refractive index.

The complex refractive index of our MoS_2 in Figure 3.8 exhibits a semiconducting behavior. In the visible and near-infrared regions of the spectrum, MoS_2 exhibits moderate absorption losses due to its semiconducting nature. This absorption is reflected with the imaginary part showing notable variation as the wavelength

changes, leading to reduced reflectivity compared to metals but higher reflectivity than dielectrics (Figure 1.2.5). The graph also shows a moderate drop or a small plateau in the real part of the refractive index starting at the end of point B (Figure 1.2.5).

The n and k values are consistent with the reported literature data Islam et al. (2021) for the in-plane complex refractive index as shown in Figure 3.8. The values presented by Islam et al. in Figure 3.8 display three distinct peaks, which can be identified as A, B, and C in order of decreasing energy Komsa and Krashennnikov (2012); Kozawa et al. (2014); Qiu et al. (2013); Shi et al. (2013). The A and B peaks correspond to transitions from the spin-orbit split valence bands to the lowest conduction band at the K and K' points. On the other hand, the C peak arises from the transition between the valence band and the conduction band within a specific region of the Brillouin zone, between the Λ point to the Γ point Kozawa et al. (2014); Qiu et al. (2013); Yu et al. (2015). The position of the peaks blue shifts as the number of layers decreases. The A and B exciton doublet peaks appear blended into a single peak, again due to possible Sulfur vacancies (Section 3.5). The thickness dependence of peak size and location is thoroughly investigated by Yu et al. Yu et al. (2015) and Song et al. Song et al. (2019) and attributed to decreasing excitonic binding, increasing joint density of states, and increasing mass density with the relative increase in film thickness. Islam et al. research on MoS₂ indicated that the refractive index of thicker films varies with light polarization, a property known as birefringence, for which they developed a specific analysis method Islam et al. (2021).

Given the polycrystalline nature of the MoS₂ films, as evidenced by XRD (Section 3.1) analysis, the optical response is influenced by a combination of in-plane and out-of-plane dielectric components. However, due to the thin-film geometry and the anisotropic electronic structure of MoS₂, the in-plane component is anticipated to play a more substantial role in the dielectric behavior. The excitation of vertical dipoles in such ultra-thin films remains challenging, which can lead to a lesser contribution from the out-of-plane dielectric function to the overall optical response Tompkins and Irene (2005); Yu et al. (2015).

3.2.2 Analysis of the Optical Properties Of ZrN

In Section 1.5.3, we explored the fabrication challenges and implications associated with the selected TMN substrate ZrN, focusing on factors such as the *presence*

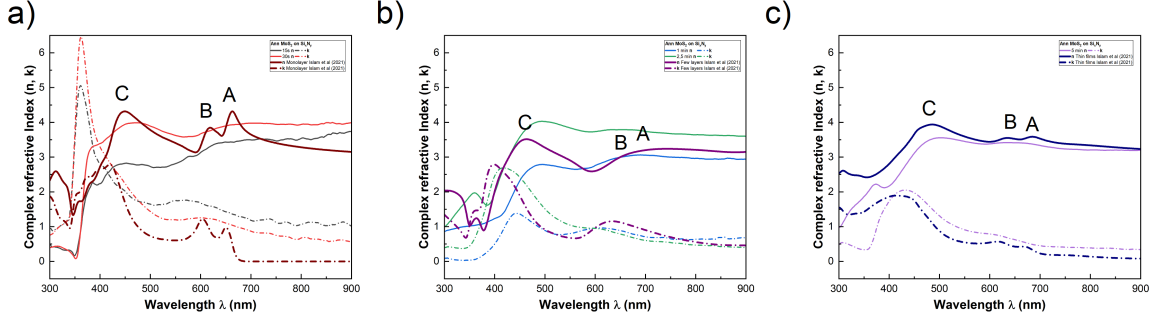


Figure 3.8 – Complex refractive index of different deposition times of MoS₂ compared with the experimental results of a) monolayer b) few layers, c) thin films samples of MoS₂ reported at Islam et al. (2021).

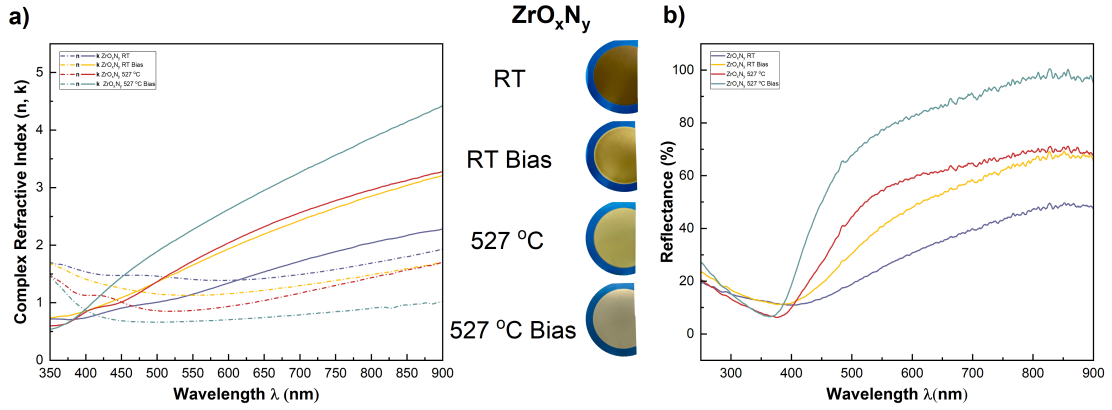


Figure 3.9 – a) The complex refractive index (n,k) and b) the reflectance of ZrO_xN_y at RT , RT Bias, 527 °C, 527 C °C Bias

of oxygen, substrate temperature, and substrate bias. A primary concern throughout the project was reducing oxygen contamination to ensure the production of materials of sufficient purity to serve as a back reflector for our MoS₂. Past Rutherford Backscattering (RBS) measurements (Section 3.5) done at LNM showed that a higher oxygen content negatively affected the metallic optical properties. This enhancement is crucial for ensuring effective reflectivity, which is vital for observing color changes indicative of alterations in the optical properties of MoS₂ arising from thickness variations. By adjusting deposition parameters like substrate temperature, applying an RF bias on the substrate, and further reducing the oxygen content in the ZrN films, the possibility of adding yttrium as an oxygen gatherer was explored.

As explained in Section 1.2.5, optically, a material is defined as metallic when the real part of its permittivity is less than zero ($\epsilon_1 = n^2 - k^2 \leq 0$) (Section 1.2.5). This

condition is met at wavelengths where k exceeds n , marking the optical transition from dielectric to metallic behavior. It is well-established that there is a significant correlation between the wavelength at which a metallic shift is observed and the inherent ability of a material to exhibit ideal metallic characteristics, which are typified by low electrical resistivity. Figure 3.9 **a)** illustrates the complex refractive index of the deposited ZrO_xN_y via a physical vapor deposition technique (magnetron sputtering) as discussed in Section 2.1.1 under various conditions: RT, RT Bias, 527 °C, and 527 °C Bias. The figure highlights the transition point's wavelength, closely related to the bias and temperature applied. While the RT -roughly 25 °C-lacks a discernible transition point, being hard to establish an effective metallic behavior, samples deposited at 527 °C reflect more light as shown in Figure 3.9 **b)**, indicating a stronger metallic nature.

Obtaining the right ZrN in the absence of high temperatures where both the Zr target and the MoS_2 were present inside the chamber posed challenges: elevating the substrate temperature was not feasible due to safety considerations and the need to protect the integrity of the MoS_2 target. One significant risk was sulfurization because of the MoS_2 being heated. This could lead to the unwanted formation of certain compounds on the material's surface. Faced with these constraints, our team explored alternative methods to optimize the deposition without increasing the temperature.

Even though we observed that higher temperatures generally led to better metallic behavior, the ZrO_xN_y RT Bias showed comparable behavior in regards to their optical properties to the 527 °C ZrO_xN_y as shown in Figure 3.9 **a)**, **b)**. It met our requirements as a substrate for MoS_2 and was suitable for assembling our HMMs structures that will be discussed in Section 3.4. We employed yttrium plasma as an oxygen gatherer with a closed substrate shutter so that just traces of Y could be present, improving the optical properties of ZrN. Because of this, the final MoS_2 -ZrN bilayers were deposited with yttrium mounted as another target. It is worth noting that, upon visual inspection of the samples shown in Figure 3.9, there is a clear increase in reflectivity when both a bias is applied and instead of raising the temperature ensuring the presence of Yttrium. This enhanced reflectiveness suggests reduced oxygen contamination, evident from the brighter coloration of the samples, which will be discussed in the next section.

3.2.3 Reflectance spectrum of MoS₂–ZrN composite

By modifying the reflectivity of ZrN surface by coating it with MoS₂ films of a few nanometres thickness, we can create a broadband absorption resonances with the spectral position determined by the film thickness. The MoS₂ deposited on the ZrN/Si₃N₄–SiO₂–Si substrate exhibit different colors, as shown in Figure 3.10 b) the colors exhibited by the MoS₂ layers depend strongly on their thicknesses. Previously, it has been shown that a highly absorptive thin film placed on a highly reflective substrate can exhibit different colors that strongly depend on the thickness of the film Kats et al. (2013a,b); Kats and Capasso (2014). The wide optical absorption band influences the color by suppressing the reflectivity in a portion of the visible spectrum. Figure 3.8 elucidates the suitability of MoS₂ for this application, attributed to its prominent absorption qualities in the visible range. A detailed investigation reveals the complex relationships between layer thickness, the process of annealing, and the bandgap transitioning from indirect to direct when going from bulk to 2D regimes, resulting in optical properties manifestations.

In layered MoS₂, the change in reflectivity is mainly due to its electronic properties, notably the transition from a direct bandgap in monolayers (about 1.9 eV) to an indirect bandgap in bulk form (around 1.2 eV). This transition affects how MoS₂ interacts with light: Electrons can directly absorb photons and jump from the valence to the conduction band, leading to efficient light absorption and reduced reflectivity. As MoS₂ transitions to an indirect bandgap in thicker layers, this direct absorption process becomes less efficient, resulting in increased reflectivity. (Mak et al. (2010); Splendiani et al. (2010). Although adding more layers increases material thickness, this physical aspect plays a less significant role compared to the bandgap change in influencing reflectivity, as highlighted in various studies (Li et al. (2012); Wang et al. (2012))

In Figure 3.10 b) as MoS₂ layers are deposited, a captivating interference-driven color progression emerges with increasing thickness. From the foundational gold color from the ZrN, transition to brown, shift to red-violet, progress to purple, deepen to blue, and finally culminate in a lighter shade of blue/gray. The underlying mechanism for these color changes is rooted in optical interference patterns. The varying thicknesses of MoS₂ layers combined with their specific refractive indices and the underlying ZrN substrate result in constructive and destructive interference of reflected light waves, creating the observed color shifts. The calculated reflection spectra corresponding to the measurements in Figure 3.10 a) are obtained by using

TMA (1.4.2) with the ellipsometry-extracted (n, k) optical properties (Section ?? Figure A.1) and both the measured and calculated reflectivity are consolidated in Figure 2.3.3 c), where the dash-dotted lines belong to the *Mathematica* simulated results for the reflectance using TMA, compared with the experimental reflectance measurements, confirming not only the accuracy of the optical properties measured to feed the TMA code but also the good agreement between the experimental and simulated reluctance reflectance.

Post deposition annealing in Figure 3.10 d)) (Section 2.2) in vacuum at 485 °C gave a difference in reflectance. The TMA calculations with the (n, k) ellipsometry-extracted optical properties confirm that the shift upon annealing is due to phase-dependent changes in the optical properties and show that these reflectance minima are due to near-perfect absorption (absorbance < 1%). Coincidentally, increasing the thickness of MoS₂ also results in a redshift. Figure 3.10 c), d) shows good agreement is obtained between the experimental data and the calculations. In Figure 3.10 e), f), the contour plots depict the relationship between Thickness, Wavelength, and Reflectance both before and after annealing. These plots provide a clear illustration of the shift to the right as the thickness increases. It is important to note that beyond a certain MoS₂ thickness, the interference patterns that define the color transitions in thinner samples become indistinguishable. This indicates the material's transition to behavior dominated by its inherent optical properties rather than interference effects.

3.3 Electrical Characterization

In our study, we observed that annealing leads to notable changes in the optical properties of MoS₂, which can be attributed to the transition from an amorphous to a crystalline structure. Our objective is to explore this amorphous-to-crystalline transition in depth and assess its impact on the electrical properties of MoS₂ films with varying thicknesses.

We investigated three samples of sputtered MoS₂ thin films, deposited for 10, 15, and 20 minutes on ZrN and Si_xN_y substrates. These samples were annealed at temperatures of 177 °C, 252 °C, 327 °C, 477 °C, and 627 °C. Across all samples, we observed a consistent shift in the reflectance minimum and an intriguing variation in resistivity with different thicknesses, particularly in both amorphous and crystalline forms annealed at 477 °C. Additionally, we noted changes in resistivity at various

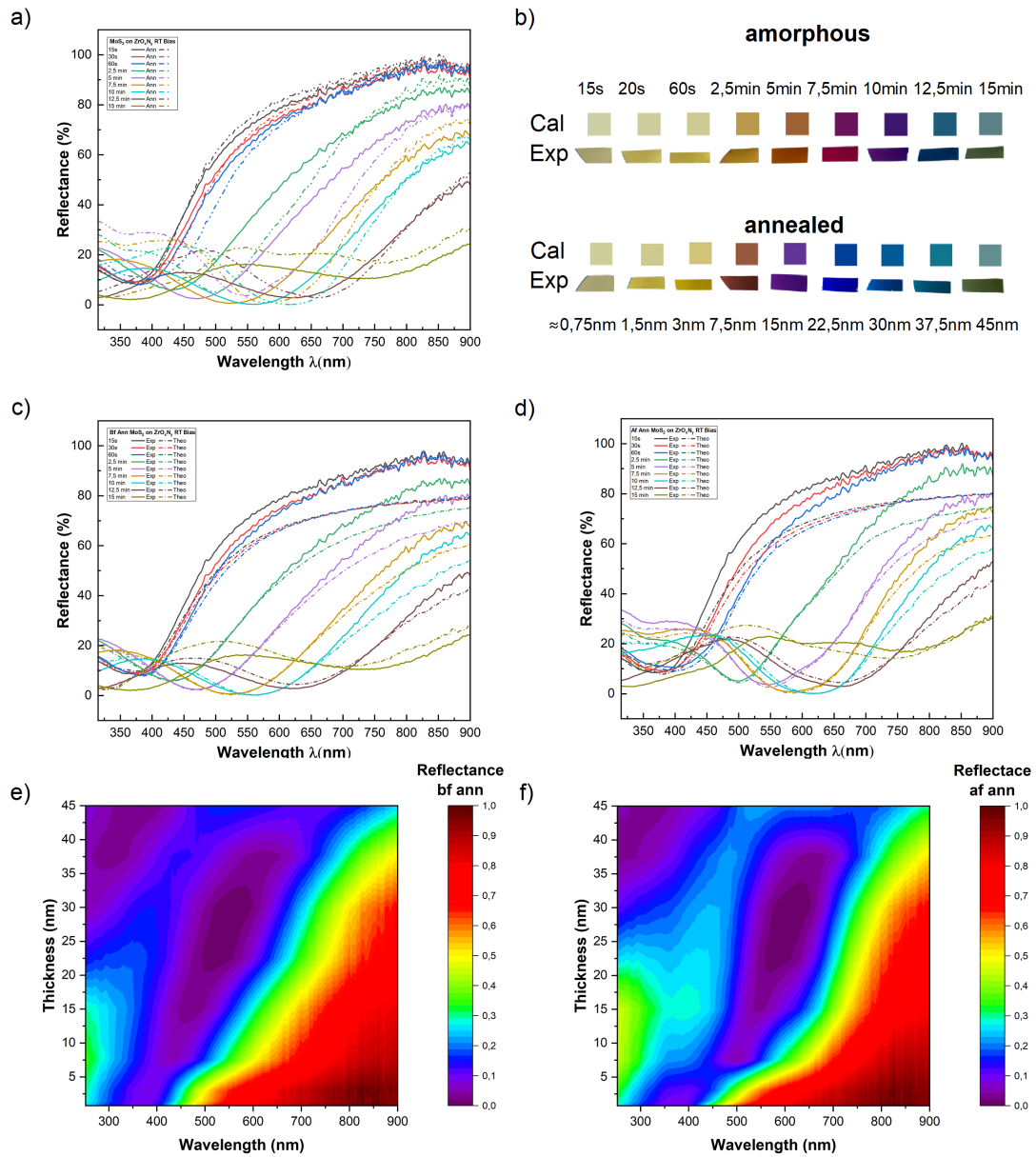


Figure 3.10 – **a)** Reflectance spectra of coated MoS₂ on ZrN RT Bias for 15 s, 30 s, 60 s, 2.5 min, 5 min, 7.5 min, 10 min, 12.5 min, 15 min deposition time. The solid lines show the as-deposited (amorphous) MoS₂, while the dotted lines show the reflectance spectra of the annealed samples at 485°C. **b)** Photographs of the fabricated (unshaped rectangles) and simulated (squares) samples of MoS₂ on top of ZrN of different thicknesses, ranging from very few-layers MoS₂ to bulk MoS₂ before (top) and after annealing (bottom), annealing at 485 °C in vacuum. The indicated thicknesses were calculated with the deposition rate of ≈ 3 nm according to the Raman spectroscopy Section 3.1. **c)**, **d)** Reflectance spectra measurements of **a)** (solid lines) compared with the simulated reflectance (dash-dotted lines) using TMA. **c)** before annealing **d)** after annealing at 485 °C in UHV. **e)**, **f)** Contour plots illustrating the relationship of thickness, wavelength, and reflectance, **e)** before annealing and **f)** after annealing.

annealing temperatures. Reflectance measurements of the annealed samples were conducted using a ZrN substrate, while electrical characterization was performed on Si_xN_y substrates. This choice was made to avoid any interference in the measurements, as Silicon Nitride (Si_3N_4) and Silicon Dioxide (SiO_2) are typically insulators and do not conduct electricity under standard conditions. This ensured that the resistivity measurements were exclusive to the MoS_2 films (refer to Section 2.4.1 for details on the four-point probe measurement technique).

3.3.1 The temperature-dependent reflectance variation of annealed samples of MoS_2

In Figure 3.11 for all three samples, annealing shifts the reflectance minimum towards higher wavelengths as the annealing temperature increases. This figure also shows how the transition temperature between the optical properties of the as-deposited sample and those of the samples annealed at higher temperatures lies between 252°C and 327°C (Figure 3.12). It is to be noted that 485°C is the temperature at which the samples in Figures 3.2, 3.3, 3.4, 3.8, 3.10 were annealed and that the XRD results shown in Figure 3.6 correspond to the same batch of samples.

These observations suggest changes in the electronic or structural properties of MoS_2 with varying temperatures. Moving vertically across the plot reveals a clear trend: as the temperature increases, the material displays a spectrum characterized by increased reflectivity.

3.3.2 Resistance and resistivity

We evaluated the electrical properties of our films using a four-point linear probe (Section 2.4.1), as illustrated in Figure 2.5 a).

Figure 3.13 illustrates the variation in voltage (V) as a function of current (I) for MoS_2 . Importantly, we were able to confirm the linear behavior expected for the V/I curve (resistance) within the material. We then determined the respective resistivities ρ using equation 2.11 as outlined in Section 2.4. These calculations took into account the respective thicknesses w (Figure 3.10) and the appropriate correction factor referenced in Uhlir Jr. (1955); Valdes (1954); Smits (1958). The resulting data is presented in Figure 3.14 and Figure 3.15.

Figure 3.14 shows the increase in resistivity with annealing temperature. It highlights a transition temperature point of approximately 250°C K, which aligns

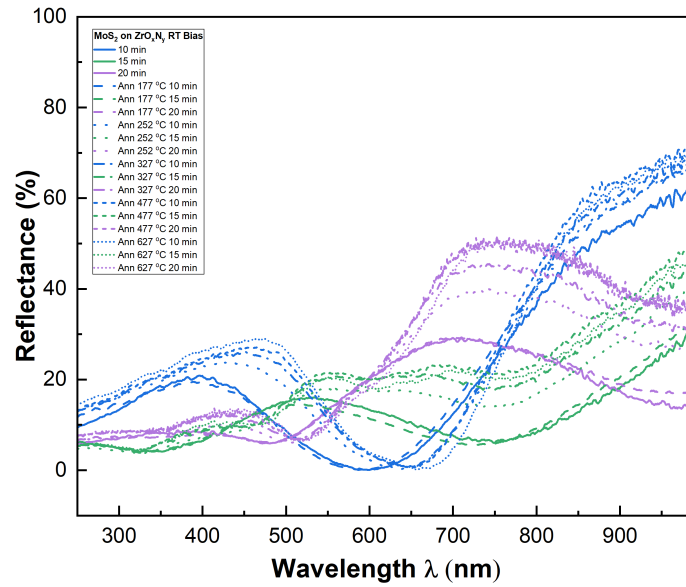


Figure 3.11 – The temperature-dependent reflectance variation of annealed samples of MoS₂ on ZrN RT Bias for deposition times of 10 min, 15 min, and 20 min. The solid lines show the spectra of the as-deposited sample, while the dotted lines show the reflectance spectra of the annealed samples at 177 °C, 252 °C, 327 °C, 477 °C, 627 °C.

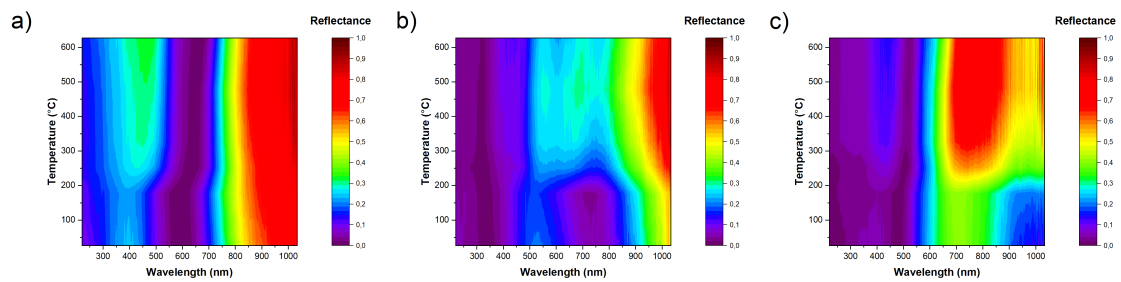


Figure 3.12 – Contour plots illustrating the relationship of Temperature, Wavelength, and Reflectance of MoS₂ on ZrN RT Bias for deposition times of a) 10 min, b) 15 min, and c) 20 min.

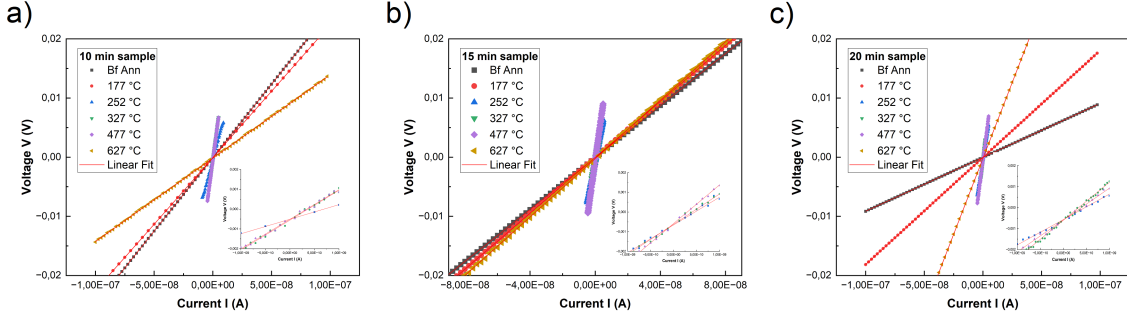


Figure 3.13 – Voltage V (V) as a function of the current I (A) for three different deposition times of **a)** 10 min, **b)** 15 min, **c)** 20 min, under varying temperatures ($^{\circ}\text{C}$).

closely to the amorphous-to-crystalline transition at roughly between 252°C and 327°C presented in Section 3.3.1 for the temperature-dependent reflectance variation and previous works presented Krbal et al. (2023). While crystallization typically results in an increase in conductivity Krbal et al. (2023), the situation in MoS_2 is the opposite. Milos Krbal et al. argued that the large electrical conductivity in its amorphous state can be traced back to an abundant number of Mo–Mo homopolar bonds Krbal et al. (2023). A significant rise in sheet resistivity is observed with the formation of Mo–S bonds, resulting from dissociating the homopolar Mo–Mo bonds between 300°C and 400°C Krbal et al. (2023). The resistivities we have computed post-annealing fall within the ranges documented in the literature for undoped MoS_2 produced via CVD Momose et al. (2018) and PVD methods Hamada et al. (2021); Hao et al. (2017); Kaindl et al. (2017).

Figure 3.15 displays the variation in resistivity for both amorphous and crystalline samples annealed at 477°C as a function of thickness. As anticipated, the amorphous samples exhibit minimal variation, given that resistivity is an intrinsic property of the material and remains independent of the thickness of our samples. However, it is notable that for the annealed samples, resistivity does increase with thickness. This is contrary to the expectation that thicker materials, providing longer paths for the charge carriers without frequent boundary collisions, should show lower resistivity. This suggests that factors other than just the limitation of carrier paths by material boundaries are influencing resistivity in these annealed samples Fuchs (1938); Mayadas and Shatzkes (1970); Xue and Gu (2016). A potential reason for this observation could be the documented enhancement in hole mobility within p-type MoS_2 as thickness decreases Zhao and Ouyang (2019). Such a decrease in resistivity with thickness has been reported in the literature for MoS_2

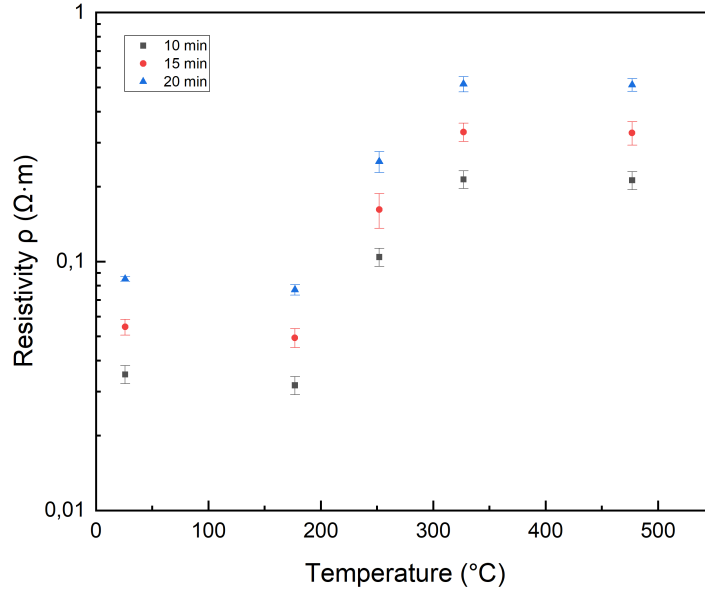


Figure 3.14 – Resistivity $\rho(\Omega \cdot \text{m})$ as a function of the temperature ($^{\circ}\text{C}$) for three different samples, with deposition times of 10 min, 15 min, and 20 min.

samples produced using various bottom-up methods Samassekou et al. (2017); Siao et al. (2018), and is also noted in other TMCs Chen et al. (2014). Siao et al. demonstrated a significant difference in electron concentration between the surface and the inner bulk of MoS_2 , with the surface electron concentration being nearly four orders of magnitude higher, exhibiting a metal-like property Siao et al. (2018). This substantial accumulation of electrons at the surface effectively increases the overall electron carrier concentration. Generally, a higher carrier concentration reduces resistivity, as more charge carriers are available for electrical conduction. This phenomenon offers a potential explanation for the thickness-dependent resistivity observed in our samples. In thinner samples, the proximity to the metal-like surface is greater, which potentially results in a decrease in the semiconducting behavior of MoS_2 . This aligns with our findings that MoS_2 nanoflakes exhibit weaker semiconducting properties than their bulk counterparts, indicating a significant deviation in electrical behavior with reduced thickness. Furthermore, the Surface Electron Accumulation (SEA) origin has been linked to sulfur vacancies on the MoS_2 surface arising from a gradual desulfurization process Siao et al. (2018). Across all investigated thicknesses, a post-annealing increase in resistivity is evident, yet the resistivity of amorphous MoS_2 consistently remains below $10 \Omega\text{cm}$ for all the thicknesses regimes as shown in Figure 3.15.

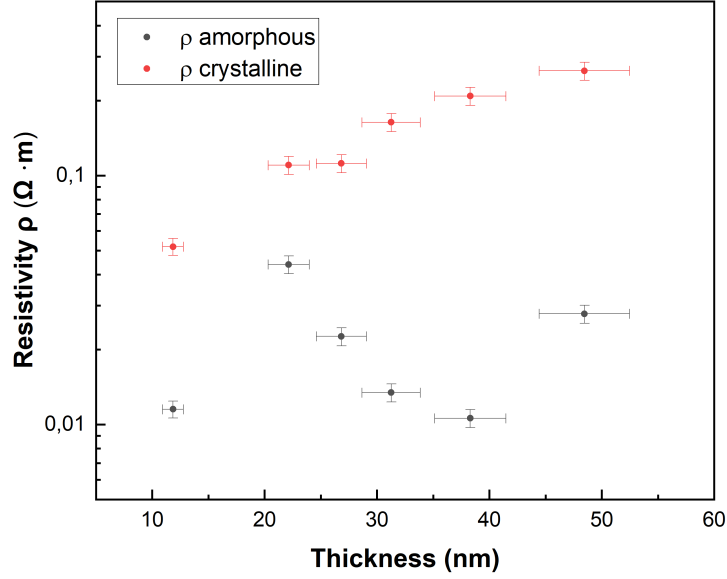


Figure 3.15 – Variation of electrical resistivity ρ ($\Omega \cdot \text{m}$) with sample thickness (nm) in both the as-deposited (black) and annealed (red) states at 485 °C.

3.4 Multilayers MoS₂–ZrN

To demonstrate the enhanced control achieved through our two-step bottom-up fabrication technique (Section 2.1.1), we designed and fabricated two correlated structures as evidence as shown in Figure 3.16. The first structure comprises three unit cells, each with a thickness of 30 nm, resulting in a total thickness of 90 nm. This configuration comprises 24 nm of ZrN and 6 nm of MoS₂ per unit cell, maintaining a ZrN filling fraction of 80 % (0.8 ff). The second structure, also totaling 90 nm in thickness, consists of six unit cells, each 15 nm thick, made up of 12 nm ZrN and 3 nm MoS₂, with the same 80 % ZrN filling fraction. Both structures were deposited on a Si₃N₄–SiO₂–Si substrate. These design parameters were meticulously chosen to induce Optical Topological Transitions (OTTs) within the visible spectrum Krishnamoorthy et al. (2012); Poddubny et al. (2013), using the (EMT) *Wolfram Mathematica* code demonstrating the precision of our deposition rate over time with the technique discussed in Section 2.1.1. We aim to show that structures with different configurations but related designs should exhibit similar optical properties (refer to Figure 3.16). In our analysis, the structures with repeating unit cells were treated as an effective medium, the substrate was considered a separate layer, and the Transfer Matrix Approach was employed to model light propagation and re-

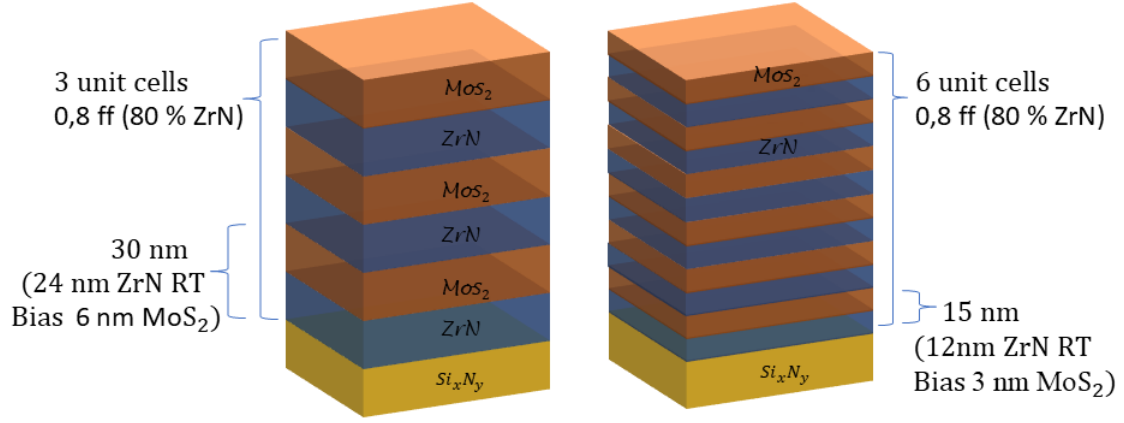


Figure 3.16 – Schematic of the designed HMMs **a)** 3 unit cells (90 nm) having a filling fraction of 0,8 ff (80 % ZrN), each one of them (30 nm) consisting of a 24 nm ZrO_xN_y RT Bias, 6 nm MoS_2 , and a Si–SiO₂–Si₃N₄ substrate. **b)** 6 unit cells (90 nm) having a filling fraction of 0,8 ff (80 % ZrN), each one of them (15 nm) consisting of a 12 nm ZrO_xN_y RT Bias, 3 nm MoS_2 , and a Si–SiO₂–Si₃N₄ substrate.

flectance through the structure.

In our OTTs, the isofrequency curve governs light propagation within a material exhibiting a significant transformation in our multilayered structures. This transformation induces pronounced anisotropy in the material’s optical properties, leading to a significant contrast between properties parallel ($\epsilon_{\parallel}$) and perpendicular ($\epsilon_{\perp}$) to the surface. Figure 3.17 presents the optical phase diagram of ZrN–MoS₂ multilayers, computed using the effective medium approximation (Section 1.3). The OTT is represented by the boundary delineating the phases. Dotted vertical lines highlight the examined composition (80 % ZrN), while horizontal dashed lines denote wavelengths at which the OTTs shift phases from an effective metal ($\epsilon_{\perp} < 0$, $\epsilon_{\parallel} < 0$) to HMM Type I, and subsequently to an effective dielectric ($\epsilon_{\perp} > 0$, $\epsilon_{\parallel} > 0$). In essence, at wavelengths below approximately 400 nm, it is expected to behave as an effective metal, while at wavelengths exceeding roughly 500 nm to take an effective dielectric behavior.

We have experimentally observed the transition between optical topologies by measuring the rP/rS ratio as shown in Figure 3.18. The propagation of hyperbolic modes is limited to p-polarized light Hoffman et al. (2007); Ferrari et al. (2015). This is due to the alignment of the electric field in p-polarized light (transverse magnetic mode) with the plane of incidence, effectively interacting with the anisotropic permittivity tensor of our multilayers, which is necessary for hyperbolic dispersion. In contrast, s-polarized light (transverse electric mode), with its electric field perpen-

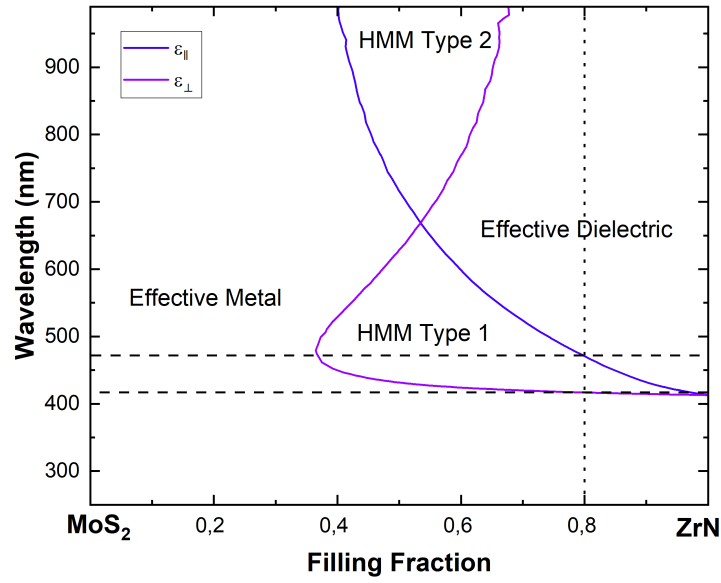


Figure 3.17 – Optical phase diagram using EMT to predict the effective behavior of the layered metamaterial (ZrN–MoS₂ (80 % ZrN)). It can behave as an effective metal ($\epsilon_{\perp} < 0$, $\epsilon_{\parallel} < 0$), effective dielectric ($\epsilon_{\perp} > 0$, $\epsilon_{\parallel} > 0$), effective HMM type I ($\epsilon_{\perp} < 0$, $\epsilon_{\parallel} > 0$), or effective HMM type II ($\epsilon_{\perp} > 0$, $\epsilon_{\parallel} < 0$) depending on the filling fraction of metal and the wavelength of the incident light. The OTT lies at the line separating the phases. The dotted vertical lines illustrate the measured composition, and the horizontal dashed lines represent the wavelengths at which the OTTs change phases from an effective metal to an HMM Type I to an effective dielectric.

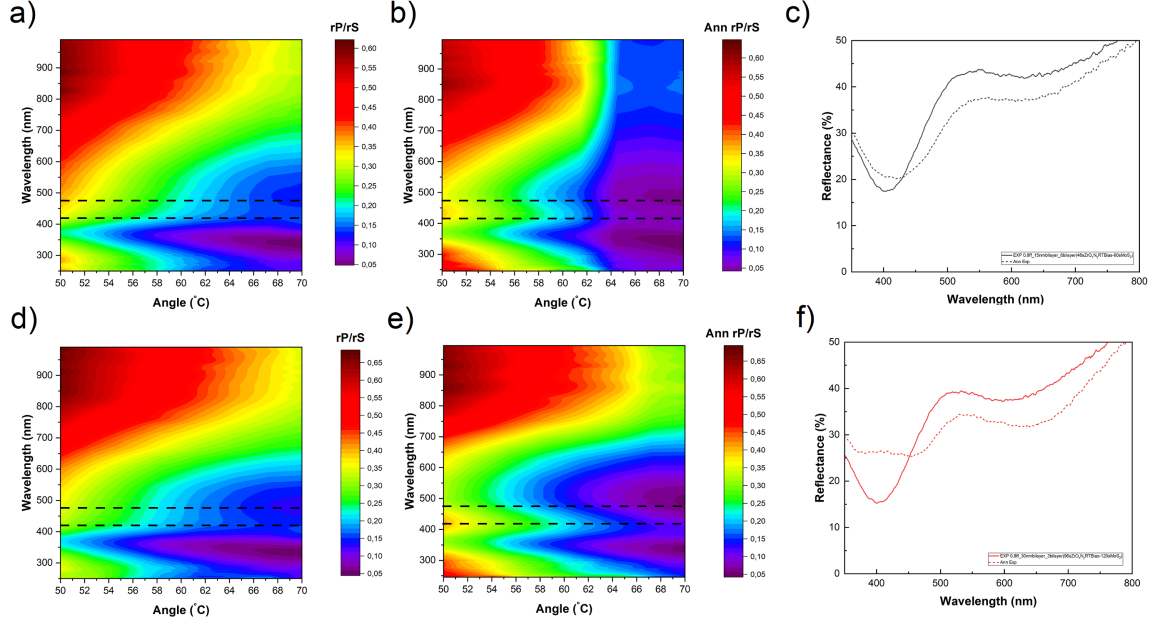


Figure 3.18 – rP/rS measured experimentally as function of wavelength and angle of incidence for a (80 % ZrN) multilayer ($ZrN-MoS_2$), three unit cells (90 nm), 30 nm each, (24 nm ZrN and 6 nm MoS_2). **a)** as-deposited, **b)** annealed at 485 °C and **c)** experimental (dotted lines) and simulated (bold lines) reflectance at normal incidence using TMA. And a six unit cells (90 nm), 15 nm each, (12 nm ZrN and 3 nm MoS_2). **d)** as-deposited, **e)** annealed at 485 °C and **f)** experimental (dotted lines) and simulated (bold lines) reflectance at normal incidence using TMA. The dashed horizontal lines indicates the wavelength at which the transition between the effective metal, HMM Type I and effective dielectric is occurs.

dicular to the incidence plane, fails to support these modes. This highlights the critical role of anisotropy in HMMs for their distinct optical behaviors, with hyperbolic modes exclusive to p-polarized light Hoffman et al. (2007); Podolskiy and Narimanov (2005); Ferrari et al. (2015). The transition from the Type I HMM phase to the dielectric phase, prompted by the shift from a negative to a positive $\epsilon_{\perp}$, is expected to cause a discontinuity in the pseudo-Brewster angle Hoffman et al. (2007); Ferrari et al. (2015); Cho et al. (2021). Our measurements confirm this discontinuity around $\lambda=475$ nm, as illustrated in Figure 3.18 **b)**, **e)**. Figure 3.18 **c)**, **f)** contrasts the measured reflectance at normal incidence with reflectance calculated using Transfer Matrix methods for the geometrical parameters shown in Figure 3.16 finding a pretty good agreement. Our technique allowed us to use our deposited films in more complex structures like MoS_2 -based HMMs, and we expect this to pave the way to MoS_2 functional devices.

Chapter 4

Conclusions and outlook

This study demonstrates the advantages of using magnetron sputtering for depositing MoS₂, focusing on its ability to reveal the material’s unique properties. We have proposed an innovative two-step bottom-up fabrication technique to synthesize wafer-scale, high-quality, and layer-controlled MoS₂ films suitable for large-scale fabrication. This process allows for the creation of MoS₂ in both its amorphous and crystalline forms, ranging from bulk, few layers, and ultra-thin layers (2D ranges), allowing us to study regimes that are not fully exploited. Notably, the quality of these films is comparable to those produced by more conventional methods. Our work contributes to developing new MoS₂-based devices.

We designed a *Mathematica* code based on Fresnel equations using *TMA* and the extracted-ellipsometry optical properties of our materials to simulate the reflectance and a complete color palette by exploiting the freedom in substrate choice, control over thickness, and the possibility of depositing amorphous MoS₂ that our deposition technique provides. A subsequent annealing step led to crystallization. Consequently, we aligned the observed optical properties from both amorphous and crystallized experiments with our simulations, noting an exceptional concordance. By understanding the change in reflectance due to crystallization, we could correlate the color changes with the electrical properties. To extend this mechanism to thinner films and show the versatility of our fabrication route, we designed a second *Mathematica* code using *EMT*; we explored different parameters such as filling fraction, structure, and unit cell thickness, and produced a MoS₂-based hyperbolic metamaterial and used it as a platform to demonstrate this optical properties correlation and our technique’s potential in fabricating complex structures.

Our findings reveal the functional attributes of amorphous and crystalline MoS₂ over varying thicknesses. Furthermore, they present a promising pathway for multiphase wafer-scale fabrication of MoS₂ and MoS₂-based architectures. We expect this study to contribute to developing functional devices based on MoS₂.

Our research indicates promising directions for future work in developing and applying the MoS₂, but certain concerns must be addressed for its desired potential to be achieved.

Industrial Scalability: The main goal is to scale our two-step fabrication process for industrial use, focusing on maintaining film quality and uniformity over larger scales, which will be essential for commercial viability.

Polycrystalline MoS₂ Improvement: We aim to refine the crystallization process of polycrystalline MoS₂, focusing on controlling grain size and orientation to enhance its electronic and optical performance, particularly in electronics and optoelectronics.

Substoichiometry and Sulfur Vacancies: A key area of future research is addressing sulfur vacancies in MoS₂, developing methods to control these vacancies during deposition. This could lead to improved electrical and optical properties and new device functionalities.

Our technique shows potential for industrial-scale implementation, provided the challenges like polycrystalline structure and substoichiometry are effectively managed. Overcoming these issues is crucial for enabling broader use of MoS₂ in technology, contributing significantly to material science advancements.

Bibliography

- Aissani, L., Alhussein, A., Zia, A. W., Mamba, G., and Rtimi, S. (2022). Magnetron Sputtering of Transition Metal Nitride Thin Films for Environmental Remediation. *Coatings*, 12(11).
- Al-Ghiffari, A. D., Ludin, N. A., Davies, M. L., Yunus, R. M., and Suait, M. S. (2022). Systematic review of molybdenum disulfide for solar cell applications: Properties, mechanism and application. *Materials Today Communications*, 32:104078.
- Alev, O. and Goldenberg, E. (2023). Nanostructured MoS₂ thin films: Effect of substrate temperature on microstructure, optical, and electrical properties. *Journal of Vacuum Science & Technology A*, 41(3):033408.
- Alexander, A.-M. and Hargreaves, J. S. J. (2010). Alternative catalytic materials: carbides, nitrides, phosphides and amorphous boron alloys. *Chem. Soc. Rev.*, 39(11):4388–4401. Publisher: The Royal Society of Chemistry.
- Ashcroft, N. W. and Mermin, N. D. (1976). *Solid State Physics*. Cengage Learning, New York, 1st edition.
- Aslanzadeh, S. A. (2018). Transition metal-metal oxide hybrids as versatile materials for hydrogen storage. *Chinese Journal of Physics*, 56(5):1917–1924.
- Bususka, T. F., Curry, J. F., Dugger, M. T., Jones, M. R., DelRio, F. W., Lu, P., Xin, Y., Grejtak, T., Chrostowski, R., Mangolini, F., Strandwitz, N. C., Chowdhury, M. I., Doll, G. L., and Krick, B. A. (2022). Quality Control Metrics to Assess MoS₂ Sputtered Films for Tribological Applications. *Tribol Lett*, 70(4):103.
- Baker, M. J., Hughes, C. S., and Hollywood, K. A. (2016). Raman spectroscopy. *Biophotonics: Vibrational Spectroscopic Diagnostics*. Publisher: Morgan & Claypool Publishers.
- Balogun, M.-S., Qiu, W., Wang, W., Fang, P., Lu, X., and Tong, Y. (2015). Recent advances in metal nitrides as high-performance electrode materials for energy storage devices. *Journal of Materials Chemistry A*, 3(4):1364–1387.
- Banwell, C. N. and McCash, E. M. (1994). *Fundamentals of Molecular Spectroscopy*. McGraw-Hill.
- Benameur, M. M., Radisavljevic, B., HÄ©ron, J. S., Sahoo, S., Berger, H., and Kis, A. (2011). Visibility of dichalcogenide nanolayers. *Nanotechnology*, 22(12):125706.

- Bertrand, P. A. (1991). Surface-phonon dispersion of MoS_2 . *Phys. Rev. B*, 44(11):5745–5749. Publisher: American Physical Society.
- Biehs, S.-A., Tschikin, M., and Ben-Abdallah, P. (2012). Hyperbolic Metamaterials as an Analog of a Blackbody in the Near Field. *Phys. Rev. Lett.*, 109(10):104301. Publisher: American Physical Society.
- Bolotin, K. I., Sikes, K. J., Jiang, Z., Klima, M., Fudenberg, G., Hone, J., Kim, P., and Stormer, H. L. (2008). Ultrahigh electron mobility in suspended graphene. *Solid State Communications*, 146(9):351–355.
- Bromley, R. A. (1971). The lattice vibrations of the MoS_2 structure. *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics*, 23(186):1417–1427. Publisher: Taylor & Francis.
- Bruggeman, D. (1935). Calculation of various physics constants in heterogenous substances I Dielectricity constants and conductivity of mixed bodies from isotropic substances. *Annalen der Physik*, Vol. 416, No. 7, pp. 636–664.
- Buck, V. (1986). Structure and density of sputtered MoS_2 -films. *Vacuum*, 36(1):89–94.
- Byrnes, S. J. (2020). Multilayer optical calculations. arXiv:1603.02720 [physics].
- Cai, W., Chettiar, U. K., Kildishev, A. V., and Shalaev, V. M. (2007). Optical cloaking with metamaterials. *Nature Photon*, 1(4):224–227.
- Cai, W. and Shalaev, V. (2010). *Optical Metamaterials: Fundamentals and Applications*. Springer, New York, NY.
- Cao, P., Peng, J., Liu, S., Cui, Y., Hu, Y., Chen, B., Li, J., and Zhai, M. (2017). Tuning the Composition and Structure of Amorphous Molybdenum Sulfide/Carbon Black Nanocomposites by Radiation Technique for Highly Efficient Hydrogen Evolution. *Sci Rep*, 7(1):16048. Number: 1 Publisher: Nature Publishing Group.
- Chakraborty, B., Matte, H. S. S. R., Sood, A. K., and Rao, C. N. R. (2013). Layer-dependent resonant Raman scattering of a few layer MoS_2 . *Journal of Raman Spectroscopy*, 44(1):92–96.
- Chambers, S. A., Thevuthasan, S., Farrow, R. F. C., Marks, R. F., Thiele, J. U., Folks, L., Samant, M. G., Kellock, A. J., Ruzyski, N., Ederer, D. L., and Diebold, U. (2001). Epitaxial growth and properties of ferromagnetic co-doped TiO_2 anatase. *Applied Physics Letters*, 79(21):3467–3469.
- Chang, Y.-H., Zhang, W., Zhu, Y., Han, Y., Pu, J., Chang, J.-K., Hsu, W.-T., Huang, J.-K., Hsu, C.-L., Chiu, M.-H., Takenobu, T., Li, H., Wu, C.-I., Chang, W.-H., Wee, A. T. S., and Li, L.-J. (2014). Monolayer MoSe_2 Grown by Chemical Vapor Deposition for Fast Photodetection. *ACS Nano*, 8(8):8582–8590. Publisher: American Chemical Society.
- Chen, J. (1996). Carbide and nitride overlayers on early transition metal surfaces: Preparation, characterization, and reactivities. *Chemical Reviews*, 96(4):1477–1498.

- Chen, Q., Gong, N., Zhu, T., Yang, C., Peng, W., Li, Y., Zhang, F., and Fan, X. (2022). Surface Phase Engineering Modulated Iron-Nickel Nitrides/Alloy Nanospheres with Tailored d-Band Center for Efficient Oxygen Evolution Reaction. *Small*, 18(4):e2105696.
- Chen, R.-S., Tang, C.-C., Shen, W.-C., and Huang, Y.-S. (2014). Thickness-dependent electrical conductivities and ohmic contacts in transition metal dichalcogenides multilayers. *Nanotechnology*, 25(41):415706. Publisher: IOP Publishing.
- Chhowalla, M., Shin, H. S., Eda, G., Li, L.-J., Loh, K. P., and Zhang, H. (2013). The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat Chem*, 5(4):263–275.
- Chiappe, D., Scalise, E., Cinquanta, E., Grazianetti, C., van den Broek, B., Fanciulli, M., Houssa, M., and Molle, A. (2014). Two-Dimensional Si Nanosheets with Local Hexagonal Structure on a MoS₂ Surface. *Advanced Materials*, 26(13):2096–2101. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.201304783>.
- Chirayil, C., Abraham, J., Mishra, R., George, S., and Thomas, S. (2017). Instrumental Techniques for the Characterization of Nanoparticles. In *Thermal and Rheological Measurement Techniques for Nanomaterials Characterization*, pages 1–36. Journal Abbreviation: Thermal and Rheological Measurement Techniques for Nanomaterials Characterization.
- Cho, H., Yang, Y., Lee, D., So, S., and Rho, J. (2021). Experimental demonstration of broadband negative refraction at visible frequencies by critical layer thickness analysis in a vertical hyperbolic metamaterial. *Nanophotonics*, 10(15):3871–3877. Publisher: De Gruyter.
- Christy, R. I. and Ludwig, H. R. (1979). R.f. sputtered MoS₂ parameter effects on wear life. *Thin Solid Films*, 64(2):223–229.
- Chung, J. W., Dai, Z. R., and Ohuchi, F. S. (1998). WS₂ thin films by metal organic chemical vapor deposition. *Journal of Crystal Growth*, 186(1):137–150.
- Coleman, J. N., Lotya, M., O'Neill, A., Bergin, S. D., King, P. J., Khan, U., Young, K., Gaucher, A., De, S., Smith, R. J., Shvets, I. V., Arora, S. K., Stanton, G., Kim, H.-Y., Lee, K., Kim, G. T., Duesberg, G. S., Hallam, T., Boland, J. J., Wang, J. J., Donegan, J. F., Grunlan, J. C., Moriarty, G., Shmeliov, A., Nicholls, R. J., Perkins, J. M., Grieveson, E. M., Theuvsen, K., McComb, D. W., Nellist, P. D., and Nicolosi, V. (2011). Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science*, 331(6017):568–571. Publisher: American Association for the Advancement of Science.
- Cortes, C. L., Newman, W., Molesky, S., and Jacob, Z. (2014). Corrigendum: Quantum nanophotonics using hyperbolic metamaterials (2012 J. Opt. 14 063001). *J. Opt.*, 16(12):129501. Publisher: IOP Publishing.
- CreaTec (2017). RTA System, rapid thermal annealing system for a wide range of applications. https://www.createc.de/media/resources/Data%20Sheet/Growth%20System/data_sheet_RTASystem_06.pdf. Accessed: 2023-04-18.

- Dines, M. B. (1975). Lithium intercalation via n-Butyllithium of the layered transition metal dichalcogenides. *Materials Research Bulletin*, 10(4):287–291.
- Domagala, R. F., McPherson, D. J., and Hansen, M. (1956). System Zirconium-Nitrogen. *JOM*, 8(2):98–105.
- DOMINGUEZ ORDONEZ, C. (2021). Electronic coupling in nickelate-based superlattices. 10. 13097/archive-ouverte/unige:161723. Accessed: 2023-04-18.
- Donarelli, M., Bisti, F., Perrozzi, F., and Ottaviano, L. (2013). Tunable sulfur desorption in exfoliated MoS₂ by means of thermal annealing in ultra-high vacuum. *Chemical Physics Letters*, 588:198–202.
- Dumcenco, D., Ovchinnikov, D., Marinov, K., LaziÄ, P., Gibertini, M., Marzari, N., Sanchez, O. L., Kung, Y.-C., Krasnozhan, D., Chen, M.-W., Bertolazzi, S., Gillet, P., Fontcuberta i Morral, A., Radenovic, A., and Kis, A. (2015). Large-Area Epitaxial Monolayer MoS₂. *ACS Nano*, 9(4):4611–4620. Publisher: American Chemical Society.
- Eda, G., Yamaguchi, H., Voiry, D., Fujita, T., Chen, M., and Chhowalla, M. (2011). Photoluminescence from Chemically Exfoliated MoS₂. *Nano Lett.*, 11(12):5111–5116. Publisher: American Chemical Society.
- Eichfeld, S. M., Hossain, L., Lin, Y.-C., Piasecki, A. F., Kupp, B., Birdwell, A. G., Burke, R. A., Lu, N., Peng, X., Li, J., Azcatl, A., McDonnell, S., Wallace, R. M., Kim, M. J., Mayer, T. S., Redwing, J. M., and Robinson, J. A. (2015). Highly scalable, atomically thin WSe₂ grown via metal-organic chemical vapor deposition. *ACS Nano*, 9(2):2080–2087.
- Feng, C., Ma, J., Li, H., Zeng, R., Guo, Z., and Liu, H. (2009). Synthesis of molybdenum disulfide (MoS₂) for lithium ion battery applications. *Materials Research Bulletin*, 44(9):1811–1815.
- Ferrari, A. C., Meyer, J. C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Piscanec, S., Jiang, D., Novoselov, K. S., Roth, S., and Geim, A. K. (2006). Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.*, 97(18):187401. Publisher: American Physical Society.
- Ferrari, L., Wu, C., Lepage, D., Zhang, X., and Liu, Z. (2015). Hyperbolic metamaterials and their applications. *Progress in Quantum Electronics*, 40:1–40.
- Feynman, R. P., Leighton, R. B., and Sands, M. L. (2011). *The Feynman lectures on physics*. Basic Books, New York, new millennium ed edition. OCLC: ocn671704374.
- Fleischauer, P. D. (1984). Effects of Crystallite Orientation on Environmental Stability and Lubrication Properties of Sputtered MoS₂ Thin Films. *A S L E Transactions*, 27(1):82–88. Publisher: Taylor & Francis _eprint: <https://doi.org/10.1080/05698198408981548>.
- FOWLIE, J. (2018). Electronic and structural properties of lanio₃-based heterostructures. 10. 13097/archive-ouverte/unige:120334. Accessed: 2023-04-18.

- Frey, G. L., Elani, S., Homyonfer, M., Feldman, Y., and Tenne, R. (1998). Optical-absorption spectra of inorganic fullerenelike MS_2 ($M = Mo, W$). *Phys. Rev. B*, 57(11):6666–6671. Publisher: American Physical Society.
- Fuchs, K. (1938). The conductivity of thin metallic films according to the electron theory of metals. *Mathematical Proceedings of the Cambridge Philosophical Society*, 34(1):100–108. Publisher: Cambridge University Press.
- Gao, B., Li, X., Ding, K., Huang, C., Li, Q., Chu, P. K., and Huo, K. (2018). Recent progress in nanostructured transition metal nitrides for advanced electrochemical energy storage. *J. Mater. Chem. A*, 7(1):14–37. Publisher: The Royal Society of Chemistry.
- Garnett, J. C. M. and Larmor, J. (1997a). VII. Colours in metal glasses, in metallic films, and in metallic solutions.âII. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character*, 205(387-401):237–288. Publisher: Royal Society.
- Garnett, J. C. M. and Larmor, J. (1997b). XII. Colours in metal glasses and in metallic films. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character*, 203(359-371):385–420. Publisher: Royal Society.
- Geim, A. K. and Novoselov, K. S. (2007). The rise of graphene. *Nature Mater*, 6(3):183–191. Number: 3 Publisher: Nature Publishing Group.
- Govvyadinov, A. A. and Podolskiy, V. A. (2006). Metamaterial photonic funnels for subdiffraction light compression and propagation. *Phys. Rev. B*, 73(15):155108. Publisher: American Physical Society.
- Griffiths, D. J. (2013). *Introduction to electrodynamics*. Pearson, Boston, fourth edition edition.
- Guo, Y., Cortes, C., Molesky, S., and Jacob, Z. (2012). Broadband super-Planckian thermal emission from hyperbolic metamaterials. *Applied Physics Letters*, 101.
- Gupta, D., Chauhan, V., and Kumar, R. (2020). A comprehensive review on synthesis and applications of molybdenum disulfide (MoS_2) material: Past and recent developments. *Inorganic Chemistry Communications*, 121:108200.
- Habe, T. and Koshino, M. (2015). Spin-dependent refraction at the atomic step of transition-metal dichalcogenides. *Phys. Rev. B*, 91(20):201407. Publisher: American Physical Society.
- Hafeez, M., Gan, L., Li, H., Ma, Y., and Zhai, T. (2016a). Chemical Vapor Deposition Synthesis of Ultrathin Hexagonal $ReSe_2$ Flakes for Anisotropic Raman Property and Optoelectronic Application. *Advanced Materials*, 28(37):8296–8301.
- Hafeez, M., Gan, L., Li, H., Ma, Y., and Zhai, T. (2016b). Large-Area Bilayer ReS_2 Film/Multilayer ReS_2 Flakes Synthesized by Chemical Vapor Deposition for High Performance Photodetectors. *Advanced Functional Materials*, 26.

- Hamada, T., Tomiya, S., Tatsumi, T., Hamada, M., Horiguchi, T., Kakushima, K., Tsutsui, K., and Wakabayashi, H. (2021). Sheet Resistance Reduction of MoS₂ Film Using Sputtering and Chlorine Plasma Treatment Followed by Sulfur Vapor Annealing. *IEEE Journal of the Electron Devices Society*, 9:278–285. Conference Name: IEEE Journal of the Electron Devices Society.
- Hao, L., Liu, Y., Du, Y., Chen, Z., Han, Z., Xu, Z., and Zhu, J. (2017). Highly Enhanced H₂ Sensing Performance of Few-Layer MoS₂/SiO₂/Si Heterojunctions by Surface Decoration of Pd Nanoparticles. *Nanoscale Res Lett*, 12(1):567.
- Harbecke, B. (1986). Coherent and incoherent reflection and transmission of multilayer structures. *Appl. Phys. B*, 39(3):165–170.
- Hassel, O. (1924). VI. Über die Kristallstruktur des Molybdänoxydglanzes. *Zeitschrift für Kristallographie - Crystalline Materials*, 61(1-6):92–99. Publisher: De Gruyter (O).
- Hecht, E. (2017). *Optics*. Pearson Education, Inc, Boston, 5 ed edition.
- Hill, H. M., Rigosi, A. F., Rim, K. T., Flynn, G. W., and Heinz, T. F. (2016). Band Alignment in MoS₂/WS₂ Transition Metal Dichalcogenide Heterostructures Probed by Scanning Tunneling Microscopy and Spectroscopy. *Nano Lett*, 16(8):4831–4837.
- Hoffman, A. J., Alekseyev, L., Howard, S. S., Franz, K. J., Wasserman, D., Podolskiy, V. A., Narimanov, E. E., Sivco, D. L., and Gmachl, C. (2007). Negative refraction in semiconductor metamaterials. *Nat Mater*, 6(12):946–950.
- Hsu, C., Frisenda, R., Schmidt, R., Arora, A., de Vasconcellos, S. M., Bratschitsch, R., van der Zant, H. S. J., and Castellanos-Gomez, A. (2019). Thickness-Dependent Refractive Index of 1L, 2L, and 3L MoS₂, MoSe₂, WS₂, and WSe₂. *Advanced Optical Materials*, 7(13):1900239.
- Hwangbo, S., Hu, L., Hoang, A. T., Choi, J. Y., and Ahn, J.-H. (2022). Wafer-scale monolithic integration of full-colour micro-LED display using MoS₂ transistor. *Nat Nanotechnol*, 17(5):500–506.
- Iorsh, I., Poddubny, A., Orlov, A., Belov, P., and Kivshar, Y. S. (2012). Spontaneous emission enhancement in metal-dielectric metamaterials. *Physics Letters A*, 376(3):185–187.
- Islam, K. M., Synowicki, R., Ismael, T., Oguntoye, I., Grinalds, N., and Escarra, M. D. (2021). In-Plane and Out-of-Plane Optical Properties of Monolayer, Few-Layer, and Thin-Film MoS₂ from 190 to 1700 nm and Their Application in Photonic Device Design. *Advanced Photonics Research*, 2(5):2000180.
- Islam, Z. and Haque, A. (2021). Defects and grain boundary effects in MoS₂: A molecular dynamics study. *Journal of Physics and Chemistry of Solids*, 148:109669.
- J.A. Woollam Company, Incorporated, J. W. C. (2008). *Guide to Using WVASE 32: Spectroscopic Ellipsometry Data Acquisition and Analysis Software*. J.A. Woollam Company, Incorporated.

- J.A. Woollam Company, Incorporated, J. W. C. (2014). CompleteEASE Software Manual. https://wiki.nanotech.ucsb.edu/w/images/2/2e/CompleteEASE_Manual.pdf. Accessed: 2023-04-18.
- Jackson, J. D. (1975). Classical electrodynamics. ISBN: 9780471431329 Publisher: Wiley.
- Jackson, J. D. (1998). *Classical Electrodynamics Third Edition*. Wiley, New York, 3rd edition edition.
- Jacob, Z., Alekseyev, L. V., and Narimanov, E. (2006). Optical hyperlens : Far field imaging beyond the diffraction limit.
- Jahani, S. and Jacob, Z. (2016). All-dielectric metamaterials. *Nature Nanotech*, 11(1):23–36. Number: 1 Publisher: Nature Publishing Group.
- Jellison, G. E. (1992). Optical functions of GaAs, GaP, and Ge determined by two-channel polarization modulation ellipsometry. *Optical Materials*, 1(3):151–160.
- Joensen, P., Frindt, R. F., and Morrison, S. R. (1986). Single-layer MoS₂. *Materials Research Bulletin*, 21(4):457–461.
- Joyce, B. A. (1985). Molecular beam epitaxy. *Rep. Prog. Phys.*, 48(12):1637.
- Kaindl, R., Bayer, B. C., Resel, R., M  ller, T., Skakalova, V., Habler, G., Abart, R., Cherevan, A. S., Eder, D., Blatter, M., Fischer, F., Meyer, J. C., Polyushkin, D. K., and Waldhauser, W. (2017). Growth, structure and stability of sputter-deposited MoS₂ thin films. *Beilstein J. Nanotechnol.*, 8(1):1115–1126. Publisher: Beilstein-Institut.
- Kang, K., Chen, S., and Yang, E.-H. (2020). Synthesis of transition metal dichalcogenides. In *Synthesis, Modeling, and Characterization of 2D Materials, and Their Heterostructures*, pages 247–264. Elsevier.
- Kang, K., Xie, S., Huang, L., Han, Y., Huang, P. Y., Mak, K. F., Kim, C.-J., Muller, D., and Park, J. (2015). High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity. *Nature*, 520(7549):656–660. Number: 7549 Publisher: Nature Publishing Group.
- Kats, M. A., Blanchard, R., Genevet, P., and Capasso, F. (2013a). Nanometre optical coatings based on strong interference effects in highly absorbing media. *Nature Mater*, 12(1):20–24. Number: 1 Publisher: Nature Publishing Group.
- Kats, M. A., Byrnes, S. J., Blanchard, R., Kolle, M., Genevet, P., Aizenberg, J., and Capasso, F. (2013b). Enhancement of absorption and color contrast in ultra-thin highly absorbing optical coatings. *Applied Physics Letters*, 103(10):101104.
- Kats, M. A. and Capasso, F. (2014). Ultra-thin optical interference coatings on rough and flexible substrates. *Appl. Phys. Lett.*, 105(13):131108.
- Katsidis, C. C. and Siapkas, D. I. (2002). General transfer-matrix method for optical multi-layer systems with coherent, partially coherent, and incoherent interference. *Appl. Opt., AO*, 41(19):3978–3987. Publisher: Optica Publishing Group.

- Kavitha, A., Kannan, R., and Loganathan, S. (2014). Effect of Substrate Bias Voltage on the Physical Properties of Zirconium Nitride (ZrN) Films Deposited by Mid Frequency Reactive Magnetron Sputtering. *Int. J. Nanosci.*, 13(02):1450015. Publisher: World Scientific Publishing Co.
- Kim, H.-J., Kim, D., Jung, S., Bae, M.-H., Yun, Y. J., Yi, S. N., Yu, J.-S., Kim, J.-H., and Ha, D. H. (2018). Changes in the Raman spectra of monolayer MoS₂ upon thermal annealing. *Journal of Raman Spectroscopy*, 49(12):1938–1944. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/jrs.5476>.
- Kim, S.-G., Kim, S.-H., Park, J., Kim, G.-S., Park, J.-H., Saraswat, K. C., Kim, J., and Yu, H.-Y. (2019). Infrared Detectable MoS₂ Phototransistor and Its Application to Artificial Multilevel Optic-Neural Synapse. *ACS Nano*, 13(9):10294–10300. Publisher: American Chemical Society.
- Kittel, C. (2005). *Introduction to solid state physics*. Wiley, Hoboken, NJ, 8th ed edition.
- Koma, A., Saiki, K., and Sato, Y. (1990). Heteroepitaxy of a two-dimensional material on a three-dimensional material. *Applied Surface Science*, 41-42:451–456.
- Komsa, H.-P. and Krasheninnikov, A. V. (2012). Effects of confinement and environment on the electronic structure and exciton binding energy of MoS₂ from first principles. *Phys. Rev. B*, 86(24):241201. Publisher: American Physical Society.
- Kong, L., Wu, R., Chen, Y., Huangfu, Y., Liu, L., Li, W., Lu, D., Tao, Q., Song, W., Li, W., Lu, Z., Liu, X., Li, Y., Li, Z., Tong, W., Ding, S., Liu, S., Ma, L., Ren, L., Wang, Y., Liao, L., Duan, X., and Liu, Y. (2023). Wafer-scale and universal van der Waals metal semiconductor contact. *Nat Commun*, 14(1):1014. Number: 1 Publisher: Nature Publishing Group.
- Korobkin, D., Neuner, B., Fietz, C., Jegenyes, N., Ferro, G., and Shvets, G. (2010). Measurements of the negative refractive index of sub-diffraction waves propagating in an indefinite permittivity medium. *Opt. Express*, 18(22):22734.
- Kozawa, D., Kumar, R., Carvalho, A., Kumar Amara, K., Zhao, W., Wang, S., Toh, M., Ribeiro, R. M., Castro Neto, A. H., Matsuda, K., and Eda, G. (2014). Photocarrier relaxation pathway in two-dimensional semiconducting transition metal dichalcogenides. *Nat Commun*, 5(1):4543. Number: 1 Publisher: Nature Publishing Group.
- Krbal, M., Prikryl, J., Pis, I., Prokop, V., Rodriguez Pereira, J., and Kolobov, A. V. (2023). Anomalous electrical conductivity change in MoS₂ during the transition from the amorphous to crystalline phase. *Ceramics International*, 49(2):2619–2625.
- Krbal, M., Prokop, V., Kononov, A. A., Pereira, J. R., Mistrik, J., Kolobov, A. V., Fons, P. J., Saito, Y., Hatayama, S., Shuang, Y., Sutou, Y., Rozhkov, S. A., Stellhorn, J. R., Hayakawa, S., Pis, I., and Bondino, F. (2021). Amorphous-to-Crystal Transition in Quasi-Two-Dimensional MoS₂: Implications for 2D Electronic Devices. *ACS Appl. Nano Mater.*, 4(9):8834–8844. Publisher: American Chemical Society.

- Krishnamoorthy, H. N. S., Jacob, Z., Narimanov, E., Kretzschmar, I., and Menon, V. M. (2012). Topological transitions in metamaterials. *Science*, 336(6078):205–209.
- Kuc, A., Zibouche, N., and Heine, T. (2011). Influence of quantum confinement on the electronic structure of the transition metal sulfide $\text{TMSS}_{\{2\}}$. *Phys. Rev. B*, 83(24):245213. Publisher: American Physical Society.
- Larijani, M. M., Kiani, M., Tanhayi, M., and Majdabadi, A. (2011). Characterization of ion beam sputtered ZrN coatings prepared at different substrate temperatures. *Crystal Research and Technology*, 46(4):351–356.
- Lee, C., Yan, H., Brus, L. E., Heinz, T. F., Hone, J., and Ryu, S. (2010). Anomalous Lattice Vibrations of Single- and Few-Layer MoS_2 . *ACS Nano*, 4(5):2695–2700. Publisher: American Chemical Society.
- Lee, D., So, S., Hu, G., Kim, M., Badloe, T., Cho, H., Kim, J., Kim, H., Qiu, C.-W., and Rho, J. (2022). Hyperbolic metamaterials: fusing artificial structures to natural 2D materials. *eLight*, 2(1):1.
- Lee, Y.-H., Zhang, X.-Q., Zhang, W., Chang, M.-T., Lin, C.-T., Chang, K.-D., Yu, Y.-C., Wang, J. T.-W., Chang, C.-S., Li, L.-J., and Lin, T.-W. (2012). Synthesis of large-area MoS_2 atomic layers with chemical vapor deposition. *Adv Mater*, 24(17):2320–2325.
- Lembke, D., Allain, A., and Kis, A. (2015). Thickness-dependent mobility in two-dimensional MoS_2 transistors. *Nanoscale*, 7(14):6255–6260.
- Lenert, A., Bierman, D. M., Nam, Y., Chan, W. R., CelanoviÄ, I., SoljaÄiÄ, M., and Wang, E. N. (2014). A nanophotonic solar thermophotovoltaic device. *Nat Nanotechnol*, 9(2):126–130.
- Li, H., Zhang, Q., Yap, C. C. R., Tay, B. K., Edwin, T. H. T., Olivier, A., and Baillargeat, D. (2012). From Bulk to Monolayer MoS_2 : Evolution of Raman Scattering. *Advanced Functional Materials*, 22(7):1385–1390.
- Li, T. and Galli, G. (2007). Electronic Properties of MoS_2 Nanoparticles. *J. Phys. Chem. C*, 111(44):16192–16196.
- Li, W., Birdwell, A. G., Amani, M., Burke, R. A., Ling, X., Lee, Y.-H., Liang, X., Peng, L., Richter, C. A., Kong, J., Gundlach, D. J., and Nguyen, N. V. (2014). Broadband optical properties of large-area monolayer CVD molybdenum disulfide. *Phys. Rev. B*, 90(19):195434. Publisher: American Physical Society.
- Lin, Z., Zhao, Y., Zhou, C., Zhong, R., Wang, X., Tsang, Y. H., and Chai, Y. (2015). Controllable Growth of Large-Size Crystalline MoS_2 and Resist-Free Transfer Assisted with a Cu Thin Film. *Sci Rep*, 5(1):18596. Number: 1 Publisher: Nature Publishing Group.
- Ling, Z. P., Yang, R., Chai, J. W., Wang, S. J., Leong, W. S., Tong, Y., Lei, D., Zhou, Q., Gong, X., Chi, D. Z., and Ang, K.-W. (2015). Large-scale two-dimensional MoS_2 photodetectors by magnetron sputtering. *Opt. Express, OE*, 23(10):13580–13586. Publisher: Optica Publishing Group.

- Lipson, S. G., Lipson, H., and Tannhauser, D. S. (1995). *Optical Physics*. Cambridge University Press.
- Liu, K.-K., Zhang, W., Lee, Y.-H., Lin, Y.-C., Chang, M.-T., Su, C.-Y., Chang, C.-S., Li, H., Shi, Y., Zhang, H., Lai, C.-S., and Li, L.-J. (2012). Growth of Large-Area and Highly Crystalline MoS₂ Thin Layers on Insulating Substrates. *Nano Lett.*, 12(3):1538–1544. Publisher: American Chemical Society.
- Liu, W., Li, A., Wu, H., Long, Y., Huang, J., Deng, X., Wang, C., Wang, Q., and Wu, S. (2016). Effects of gas pressure on microstructure and performance of (Ti, Al, Zr)N coatings produced by physical vapor deposition. *Ceramics International*, 42(15):17436–17441.
- Liu, X., Tyler, T., Starr, T., Starr, A. F., Jokerst, N. M., and Padilla, W. J. (2011). Taming the Blackbody with Infrared Metamaterials as Selective Thermal Emitters. *Phys. Rev. Lett.*, 107(4):045901. Publisher: American Physical Society.
- Liu, Z., Lee, H., Xiong, Y., Sun, C., and Zhang, X. (2007). Far-Field Optical Hyperlens Magnifying Sub-Diffraction-Limited Objects. *Science*, 315(5819):1686–1686.
- Lu, Y., Li, Z., Xu, Y., Tang, L., Xu, S., Li, D., Zhu, J., and Jiang, D. (2021). Bimetallic Co-Mo nitride nanosheet arrays as high-performance bifunctional electrocatalysts for overall water splitting. *Chemical Engineering Journal*, 411:128433.
- Luo, Q., Lu, C., Liu, L., and Zhu, M. (2023). A review on the synthesis of transition metal nitride nanostructures and their energy related applications. *Green Energy & Environment*, 8(2):406–437.
- Maier, S. A. (2007). *Plasmonics: Fundamentals and Applications*. Springer US, New York, NY.
- Mak, K. F., Lee, C., Hone, J., Shan, J., and Heinz, T. F. (2010). Atomically Thin MoS₂ : A New Direct-Gap Semiconductor. *Phys. Rev. Lett.*, 105(13):136805.
- Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O. V., and Kis, A. (2017). 2D transition metal dichalcogenides. *Nat Rev Mater*, 2(8):1–15. Number: 8 Publisher: Nature Publishing Group.
- Markoš, P. and Soukoulis, C. M. (2008). *Wave Propagation: From Electrons to Photonic Crystals and Left-Handed Materials*. Princeton University Press, stu - student edition edition.
- Mascaretti, L., Barman, T., Bricchi, B. R., MÄnz, F., Li Bassi, A., Kment, rA., and Naldoni, A. (2021). Controlling the plasmonic properties of titanium nitride thin films by radiofrequency substrate biasing in magnetron sputtering. *Applied Surface Science*, 554:149543.
- Mayadas, A. F. and Shatzkes, M. (1970). Electrical-Resistivity Model for Polycrystalline Films: the Case of Arbitrary Reflection at External Surfaces. *Phys. Rev. B*, 1(4):1382–1389. Publisher: American Physical Society.
- Mazaheri, A., Lee, M., Zant, H. S. J. v. d., Frisenda, R., and Castellanos-Gomez, A. (2020). MoS₂-on-paper optoelectronics: drawing photodetectors with van der Waals semiconductors beyond graphite. *Nanoscale*, 12(37):19068–19074. Publisher: The Royal Society of Chemistry.

- McMorrow, D. and Als-Nielsen, J. (2011). *Elements of Modern X-ray Physics*. John Wiley & Sons.
- Meng, Z., Zheng, S., Luo, R., Tang, H., Wang, R., Zhang, R., Tian, T., and Tang, H. (2022). Transition Metal Nitrides for Electrocatalytic Application: Progress and Rational Design. *Nanomaterials (Basel)*, 12(15):2660.
- Molina-Sánchez, A. and Wirtz, L. (2011). Phonons in single-layer and few-layer MoS_2 and WS_2 . *Phys. Rev. B*, 84(15):155413. Publisher: American Physical Society.
- Momose, T., Nakamura, A., Daniel, M., and Shimomura, M. (2018). Phosphorous doped p -type MoS_2 polycrystalline thin films via direct sulfurization of Mo film. *AIP Advances*, 8(2):025009.
- Mrstik, B. J., Kaplan, R., Reinecke, T. L., Van Hove, M., and Tong, S. Y. (1977). Surface-structure determination of the layered compounds MoS_2 and NbSe_2 by low-energy electron diffraction. *Phys. Rev. B*, 15(2):897–900. Publisher: American Physical Society.
- Muratore, C., Hu, J. J., Wang, B., Haque, M. A., Bultman, J. E., Jespersen, M. L., Shamberger, P. J., McConney, M. E., Naguy, R. D., and Voevodin, A. A. (2014). Continuous ultrathin MoS_2 films grown by low-temperature physical vapor deposition. *Applied Physics Letters*, 104(26):261604.
- Naik, G. V., Shalaev, V. M., and Boltasseva, A. (2013). Alternative Plasmonic Materials: Beyond Gold and Silver. *Advanced Materials*, 25(24):3264–3294.
- Najmaei, S., Liu, Z., Zhou, W., Zou, X., Shi, G., Lei, S., Yakobson, B. I., Idrobo, J.-C., Ajayan, P. M., and Lou, J. (2013). Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nature Mater*, 12(8):754–759. Number: 8 Publisher: Nature Publishing Group.
- Nassau, K. (1987). The fifteen causes of color: The physics and chemistry of color. *Color Research & Application*, 12(1):4–26.
- Nefedov, I. S. and Simovski, C. R. (2011). Giant radiation heat transfer through micron gaps. *Phys. Rev. B*, 84(19):195459. Publisher: American Physical Society.
- Negara, C. (2016). *Fast Polarization State Detection by Division-of-Amplitude in a Simple Configuration Setup*.
- Nicolosi, V., Chhowalla, M., Kanatzidis, M. G., Strano, M. S., and Coleman, J. N. (2013). Liquid exfoliation of layered materials. *Science*, 340(6139).
- Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., and Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669.
- Novoselov, K. S., Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V., and Geim, A. K. (2005). Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences*, 102(30):10451–10453. Publisher: Proceedings of the National Academy of Sciences.

- Ocana-Pujol, J. L., Forster, L., Spolenak, R., and Galinski, H. (2022). Strain-Driven Thermal and Optical Instability in Silver/Amorphous-Silicon Hyperbolic Metamaterials. *Advanced Optical Materials*, 10(24):2201749.
- Oura, K., Katayama, M., Zotov, A. V., Lifshits, V. G., and Saranin, A. A. (2003). Growth of Thin Films. In Oura, K., Katayama, M., Zotov, A. V., Lifshits, V. G., and Saranin, A. A., editors, *Surface Science: An Introduction*, Advanced Texts in Physics, pages 357–387. Springer, Berlin, Heidelberg.
- Palik, E. D. (1998). *Handbook of Optical Constants of Solids*. Academic Press.
- Park, S. H., Jo, T. H., Lee, M. H., Kawashima, K., Mullins, C. B., Lim, H.-K., and Youn, D. H. (2021). Highly active and stable nickelâmolymdendum nitride (Ni₂Mo₃N) electrocatalyst for hydrogen evolution. *J. Mater. Chem. A*, 9(8):4945–4951. Publisher: The Royal Society of Chemistry.
- Parkin, W. M., Balan, A., Liang, L., Das, P. M., Lamparski, M., Naylor, C. H., RodrÃguez-Manzo, J. A., Johnson, A. T. C., Meunier, V., and DrndiÄ, M. (2016). Raman Shifts in Electron-Irradiated Monolayer MoS₂. *ACS Nano*, 10(4):4134–4142.
- Pauli, W. (1925). Äber den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren. *Z. Physik*, 31(1):765–783.
- Pendry, J. B., Schurig, D., and Smith, D. R. (2006). Controlling Electromagnetic Fields. *Science*, 312(5781):1780–1782. Publisher: American Association for the Advancement of Science.
- Penttinen, I., Molarius, J. M., Korhonen, A. S., and Lappalainen, R. (1988). Structure and composition of ZrN and (Ti,Al)N coatings. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 6(3):2158–2161.
- PJ Linstrom, W. M. (2011). Nist chemistry webbook, nist standard reference database number 69, national institute of standards and technology. Gaithersburg MD, 20899, 2011.
- Poddubny, A., Iorsh, I., Belov, P., and Kivshar, Y. (2013). Hyperbolic metamaterials. *Nature Photonics*, 7:948–957.
- Podolskiy, V. A. and Narimanov, E. E. (2005). Strongly anisotropic waveguide as a nonmagnetic left-handed system. *Phys. Rev. B*, 71(20):201101. Publisher: American Physical Society.
- Pulkin, A. and Yazyev, O. V. (2016). Spin- and valley-polarized transport across line defects in monolayer MoS₂. *Phys. Rev. B*, 93(4):041419. Publisher: American Physical Society.
- Purandare, Y., Ehiasarian, A., and Hovsepian, P. (2011). Structure and properties of ZrN coatings deposited by high power impulse magnetron sputtering technology. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 29:011004–011004.
- Qiu, D. Y., da Jornada, F. H., and Louie, S. G. (2013). Optical Spectrum of MoS₂: Many-Body Effects and Diversity of Exciton States. *Phys. Rev. Lett.*, 111(21):216805. Publisher: American Physical Society.

- Rabe, K. M., Dawber, M., Lichtensteiger, C., Ahn, C. H., and Triscone, J.-M. (2007). Modern Physics of Ferroelectrics: Essential Background. In *Physics of Ferroelectrics: A Modern Perspective*, Topics in Applied Physics, pages 1–30. Springer, Berlin, Heidelberg.
- Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V., and Kis, A. (2011). Single-layer MoS₂ transistors. *Nat Nanotechnol*, 6(3):147–150.
- Rapoport, L., Moshkovich, A., Perflyev, V., Lapsker, I., Halperin, G., Itovich, Y., and Etsion, I. (2008). Friction and wear of MoS₂ films on laser textured steel surfaces. *Surface and Coatings Technology*, 202(14):3332–3340.
- Re, M., Gouttebaron, R., Dauchot, J. P., Leclerc, P., Terwagne, G., and Hecq, M. (2003). XPS study of ZrN layers deposited by reactive magnetron sputtering. *Surface & Coatings Technology*, 174:240–245.
- Renevier, N. M., Fox, V. C., Teer, D. G., and Hampshire, J. (2000). Coating characteristics and tribological properties of sputter-deposited MoS₂/metal composite coatings deposited by closed field unbalanced magnetron sputter ion plating. *Surface and Coatings Technology*, 127(1):24–37.
- Rizzo, A., Signore, M. A., Valerini, D., Altamura, D., Cappello, A., and Tapfer, L. (2012). A study of suppression effect of oxygen contamination by bias voltage in reactively sputtered ZrN films. *Surface and Coatings Technology*, 206(10):2711–2718.
- Roman, D., Bernardi, J., Amorim, C. L. G. d., de Souza, F. S., Spinelli, A., Giacomelli, C., Figueroa, C. A., Baumvol, I. J. R., and Basso, R. L. O. (2011). Effect of deposition temperature on microstructure and corrosion resistance of ZrN thin films deposited by DC reactive magnetron sputtering. *Materials Chemistry and Physics*, 130(1):147–153.
- Rosencher, E. and Vinter, B. (2002). *Optoelectronics*. Cambridge University Press. Google-Books-ID: x54JBfP8O0AC.
- Samassekou, H., Alkabsh, A., Wasala, M., Eaton, M., Walber, A., Walker, A., Pitkäranta, O., Kordas, K., Talapatra, S., Jayasekera, T., and Mazumdar, D. (2017). Viable route towards large-area 2D MoS₂ using magnetron sputtering. *2D Mater.*, 4(2):021002. Publisher: IOP Publishing.
- SAOULA, N., Azibi, M., and Aknouche, H. (2019). The influence of substrate bias voltage on the electrochemical properties of ZrN thin films deposited by radio-frequency magnetron sputtering: Biomedical application. *Journal of Electrical Engineering*, 70:112–116.
- Shekhar, P., Atkinson, J., and Jacob, Z. (2014). Hyperbolic metamaterials: fundamentals and applications. *Nano Convergence*, 1(1):14.
- Shi, H., Pan, H., Zhang, Y.-W., and Yakobson, B. I. (2013). Quasiparticle band structures and optical properties of strained monolayer MoS₂ and WS₂. *Phys. Rev. B*, 87(15):155304. Publisher: American Physical Society.

- Shi, J., Jiang, B., Li, C., Yan, F., Wang, D., Yang, C., and Wan, J. (2020). Review of Transition Metal Nitrides and Transition Metal Nitrides/Carbon nanocomposites for supercapacitor electrodes. *Materials Chemistry and Physics*, 245:122533.
- Shi, Y., Zhou, W., Lu, A.-Y., Fang, W., Lee, Y.-H., Hsu, A. L., Kim, S. M., Kim, K. K., Yang, H. Y., Li, L.-J., Idrobo, J.-C., and Kong, J. (2012). van der Waals Epitaxy of MoS₂ Layers Using Graphene As Growth Templates. *Nano Lett.*, 12(6):2784–2791. Publisher: American Chemical Society.
- Siao, M. D., Shen, W. C., Chen, R. S., Chang, Z. W., Shih, M. C., Chiu, Y. P., and Cheng, C.-M. (2018). Two-dimensional electronic transport and surface electron accumulation in MoS₂. *Nat Commun*, 9(1):1442.
- Signore, M. A., Valerini, D., Rizzo, A., Tapfer, L., Capodieci, L., and Cappello, A. (2010). Investigation of the physical properties of ion assisted ZrN thin films deposited by RF magnetron sputtering. *J. Phys. D: Appl. Phys.*, 43(22):225401.
- Simon, D. K., TrÄ¶ger, D., Schenk, T., Dirnstorfer, I., Fengler, F. P. G., Jordan, P. M., Krause, A., and Mikolajick, T. (2016). Comparative study of ITO and TiN fabricated by low-temperature RF biased sputtering. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 34(2):021503.
- Sirota, B., Glavin, N., and Voevodin, A. A. (2019). Room temperature magnetron sputtering and laser annealing of ultrathin MoS₂ for flexible transistors. *Vacuum*, 160:133–138.
- Smith, D. R., Padilla, W. J., Vier, D. C., Nemat-Nasser, S. C., and Schultz, S. (2000). Composite Medium with Simultaneously Negative Permeability and Permittivity. *Phys. Rev. Lett.*, 84(18):4184–4187.
- Smits, F. M. (1958). Measurement of Sheet Resistivities with the Four-Point Probe. *Bell System Technical Journal*, 37(3):711–718.
- Song, B., Gu, H., Fang, M., Chen, X., Jiang, H., Wang, R., Zhai, T., Ho, Y.-T., and Liu, S. (2019). Layer-Dependent Dielectric Function of Wafer-Scale 2D MoS₂. *Advanced Optical Materials*, 7(2):1801250.
- Soo Kang, J., Park, M.-A., Kim, J.-Y., Ha Park, S., Young Chung, D., Yu, S.-H., Kim, J., Park, J., Choi, J.-W., Jae Lee, K., Jeong, J., Jae Ko, M., Ahn, K.-S., and Sung, Y.-E. (2015). Reactively sputtered nickel nitride as electrocatalytic counter electrode for dye- and quantum dot-sensitized solar cells. *Sci Rep*, 5(1):10450. Number: 1 Publisher: Nature Publishing Group.
- Spalvins, T. (1975). *Bearing Endurance Tests in Vacuum for Sputtered Molybdenum Disulfide Films*. National Aeronautics and Space Administration.
- Splendiani, A., Sun, L., Zhang, Y., Li, T., Kim, J., Chim, C.-Y., Galli, G., and Wang, F. (2010). Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.*, 10(4):1271–1275. Publisher: American Chemical Society.

- Staia, M. H., Trocelis, A., Zairi, A., Suarez, M., Puchi-Cabrera, E. S., Iost, A., and Montagne, A. (2019). Assessment of the mechanical and tribological performance of a ZrN PVD coating. *Surface Engineering*, 35(6):491–500. Publisher: Taylor & Francis _eprint: <https://doi.org/10.1080/02670844.2017.1414766>.
- Tao, J., Chai, J., Lu, X., Wong, L. M., Wong, T. I., Pan, J., Xiong, Q., Chi, D., and Wang, S. (2015). Growth of wafer-scale MoS₂ monolayer by magnetron sputtering. *Nanoscale*, 7(6):2497–2503. Publisher: The Royal Society of Chemistry.
- Timpel, M., Ligorio, G., Ghiami, A., Gavioli, L., Cavaliere, E., Chiappini, A., Rossi, F., Pasquali, L., GÃ¼risch, F., List-Kratochvil, E. J. W., Nozar, P., Quaranta, A., Verucchi, R., and Nardi, M. V. (2021). 2D-MoS₂ goes 3D: transferring optoelectronic properties of 2D MoS₂ to a large-area thin film. *npj 2D Mater Appl*, 5(1):64.
- Tompkins, H. G. and Irene, E. A., editors (2005). *Handbook of ellipsometry*. William Andrew Pub. ; Springer, Norwich, NY : Heidelberg, Germany.
- Tsai, M.-L., Su, S.-H., Chang, J.-K., Tsai, D.-S., Chen, C.-H., Wu, C.-I., Li, L.-J., Chen, L.-J., and He, J.-H. (2014). Monolayer MoS₂ heterojunction solar cells. *ACS Nano*, 8(8):8317–8322.
- Tuschel, D. (2017). Why are the Raman spectra of crystalline and amorphous solids different? 32:26–33.
- Uchida, H., Yamashita, M., Hanaki, S., and Ueta, T. (2004). Characterization of (Ti, Al)N films prepared by ion mixing and vapor deposition. *Materials Science and Engineering: A*, 387-389:758–762.
- Uhlir Jr., A. (1955). The Potentials of Infinite Systems of Sources and Numerical Solutions of Problems in Semiconductor Engineering. *Bell System Technical Journal*, 34(1):105–128.
- Valdes, L. (1954). Resistivity Measurements on Germanium for Transistors. *Proc. IRE*, 42(2):420–427.
- van der Zande, A. M., Huang, P. Y., Chenet, D. A., Berkelbach, T. C., You, Y., Lee, G.-H., Heinz, T. F., Reichman, D. R., Muller, D. A., and Hone, J. C. (2013). Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide. *Nature Mater*, 12(6):554–561. Number: 6 Publisher: Nature Publishing Group.
- Verble, J. L. and Wieting, T. J. (1970). Lattice Mode Degeneracy in MoS₂ and Other Layer Compounds. *Phys. Rev. Lett.*, 25(6):362–365.
- Verble, J. L., Wietling, T. J., and Reed, P. R. (1972). Rigid-layer lattice vibrations and van der waals bonding in hexagonal MoS₂. *Solid State Communications*, 11(8):941–944.
- Vu, Q. A., Kim, H., Nguyen, V. L., Won, U. Y., Adhikari, S., Kim, K., Lee, Y. H., and Yu, W. J. (2017). A High-On/Off-Ratio Floating-Gate Memristor Array on a Flexible Substrate via CVD-Grown Large-Area 2D Layer Stacking. *Advanced Materials*, 29(44):1703363.

- Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N., and Strano, M. S. (2012). Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature Nanotech*, 7(11):699–712. Number: 11 Publisher: Nature Publishing Group.
- Wang, S., Liu, X., and Zhou, P. (2022). The Road for 2D Semiconductors in the Silicon Age. *Advanced Materials*, 34(48):2106886. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.202106886>.
- Weil, K. S. c. and Kumta, P. r. N. (2001). Synthesis of transition metal nitride powders and coatings using alkanolamine chelated precursors. *Materials & Design*, 22(7):605–615.
- Wieting, T. J. and Verble, J. L. (1972). Interlayer Bonding and the Lattice Vibrations of $\beta - \text{GaSe}$. *Phys. Rev. B*, 5(4):1473–1479. Publisher: American Physical Society.
- Wilson, J. and Yoffe, A. (1969). The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Advances in Physics*, 18(73):193–335.
- Wood, S. and Anderson, G. (2014). Stable and metastable equilibrium: The third constraint.
- Wu, S., Deng, D., Zhang, E., Li, H., and Xu, L. (2022). CoN nanoparticles anchored on ultra-thin N-doped graphene as the oxygen reduction electrocatalyst for highly stable zinc-air batteries. *Carbon*, 196.
- Xi, S., Lin, G., Jin, L., Li, H., and Xie, K. (2019). Metallic porous nitride single crystals at two-centimeter scale delivering enhanced pseudocapacitance. *Nature Communications*, 10(1).
- Xiao, D., Liu, G.-B., Feng, W., Xu, X., and Yao, W. (2012). Coupled Spin and Valley Physics in Monolayers of MoS_2 and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.*, 108(19):196802. Publisher: American Physical Society.
- Xiao, S., Xiao, P., Zhang, X., Yan, D., Gu, X., Qin, F., Ni, Z., Han, Z. J., and Ostrikov, K. K. (2016). Atomic-layer soft plasma etching of MoS_2 . *Sci Rep*, 6:19945.
- Xie, X., Makaryan, T., Zhao, M., Van Aken, K. L., Gogotsi, Y., and Wang, G. (2016). MoS_2 Nanosheets Vertically Aligned on Carbon Paper: A Freestanding Electrode for Highly Reversible Sodium-Ion Batteries. *Advanced Energy Materials*, 6(5):1502161. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/aenm.201502161>.
- Xu, J., Yan, H., Jin, Z., and Jia, C.-J. (2019). Facile Synthesis of Stable MO_2N Nanobelts with High Catalytic Activity for Ammonia Decomposition. *Chinese Journal of Chemistry*, 37.
- Xue, W. and Gu, W. (2016). Conductivity size effect of polycrystalline metal nanowires. *AIP Advances*, 6(11):115001.
- Xue, Y., Zhang, Q., Wang, W., Cao, H., Yang, Q., and Fu, L. (2017). Opening Two-Dimensional Materials for Energy Conversion and Storage: A Concept. *Advanced Energy Materials*, 7(19):1602684. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/aenm.201602684>.

- Yang, D., Sandoval, S. J., Divigalpitiya, W. M. R., Irwin, J. C., and Frindt, R. F. (1991). Structure of single-molecular-layer MoS_2 . *Phys. Rev. B*, 43(14):12053–12056. Publisher: American Physical Society.
- Yang, F., Ma, S., Ding, K., Zhang, S., and Pendry, J. B. (2020). Continuous topological transition from metal to dielectric. *Proceedings of the National Academy of Sciences*, 117(29):16739–16742. Publisher: Proceedings of the National Academy of Sciences.
- Yang, P., Yang, H., Wu, Z., Liao, F., Guo, X., Deng, J., Xu, Q., Wang, H., Sun, J., Chen, F., Bao, W., Hu, L., Liu, Z., Chen, Y., Qiu, Z.-J., Fang, Z., Liu, R., and Cong, C. (2021). Large-Area Monolayer MoS_2 Nanosheets on GaN Substrates for Light-Emitting Diodes and Valley-Spin Electronic Devices. *ACS Appl. Nano Mater.*, 4(11):12127–12136. Publisher: American Chemical Society.
- Yang, Y.-T., Wu, H.-W., Zou, Y., Fang, X.-Y., Li, S., Song, Y.-F., Wang, Z.-H., and Zhang, B. (2022). Facile Synthesis of Monodispersed Titanium Nitride Quantum Dots for Harmonic Mode-Locking Generation in an Ultrafast Fiber Laser. *Nanomaterials*, 12(13):2280. Number: 13 Publisher: Multidisciplinary Digital Publishing Institute.
- Yao, J., Liu, Z., Liu, Y., Wang, Y., Sun, C., Bartal, G., Stacy, A. M., and Zhang, X. (2008). Optical negative refraction in bulk metamaterials of nanowires. *Science*, 321(5891):930.
- Yao, J., Yang, X., Yin, X., Bartal, G., and Zhang, X. (2011). Three-dimensional nanometer-scale optical cavities of indefinite medium. *Proceedings of the National Academy of Sciences*, 108(28):11327–11331. Publisher: Proceedings of the National Academy of Sciences.
- Yao, W., Makowski, P., Giordano, C., and Goettmann, F. (2009). Synthesis of Early-Transition-Metal Carbide and Nitride Nanoparticles through the Urea Route and Their Use as Alkylation Catalysts. *Chemistry â A European Journal*, 15(44):11999–12004. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/chem.200901496>.
- Yazyev, O. V. and Kis, A. (2015). MoS_2 and semiconductors in the flatland. *Materials Today*, 18(1):20–30.
- Yi, M. and Shen, Z. (2015). A review on mechanical exfoliation for the scalable production of graphene. *J. Mater. Chem. A*, 3(22):11700–11715.
- Youn, D. H., Han, S., Kim, J. Y., Kim, J. Y., Park, H., Choi, S. H., and Lee, J. S. (2014). Highly Active and Stable Hydrogen Evolution Electrocatalysts Based on Molybdenum Compounds on Carbon NanotubeâGraphene Hybrid Support. *ACS Nano*, 8(5):5164–5173. Publisher: American Chemical Society.
- Yu, Y., Yu, Y., Cai, Y., Li, W., Gurarslan, A., Peelaers, H., Aspnes, D. E., Van de Walle, C. G., Nguyen, N. V., Zhang, Y.-W., and Cao, L. (2015). Exciton-dominated Dielectric Function of Atomically Thin MoS_2 Films. *Sci Rep*, 5(1):16996. Number: 1 Publisher: Nature Publishing Group.

- Yun, Q., Lu, Q., Zhang, X., Tan, C., and Zhang, H. (2018). Three-Dimensional Architectures Constructed from Transition-Metal Dichalcogenide Nanomaterials for Electrochemical Energy Storage and Conversion. *Angew Chem Int Ed Engl*, 57(3):626–646.
- Zangwill, A. (2013). *Modern electrodynamics*. Cambridge University Press, Cambridge.
- Zeng, R., Yang, Y., Feng, X., Li, H., Gibbs, L. M., DiSalvo, F. J., and Abruña, H. D. (2022). Nonprecious transition metal nitrides as efficient oxygen reduction electrocatalysts for alkaline fuel cells. *Sci Adv*, 8(5):eabj1584.
- Zhan, Y., Liu, Z., Najmaei, S., Ajayan, P. M., and Lou, J. (2012). Large-Area Vapor-Phase Growth and Characterization of MoS₂ Atomic Layers on a SiO₂ Substrate. *Small*, 8(7):966–971.
- Zhang, X., Biekert, N., Choi, S., Naylor, C. H., De-Eknamkul, C., Huang, W., Zhang, X., Zheng, X., Wang, D., Johnson, A. T. C., and Cubukcu, E. (2018). Dynamic Photochemical and Optoelectronic Control of Photonic Fano Resonances via Monolayer MoS₂ Trions. *Nano Lett.*, 18(2):957–963. Publisher: American Chemical Society.
- Zhang, X., Fu, W., Tian, W., Wan, J., Zhang, H., and Wang, Y. (2020). Distorted quantum dots enhance the efficiency of alkaline oxygen electrocatalysis. *J. Mater. Chem. A*, 8(40):21173–21180. Publisher: The Royal Society of Chemistry.
- Zhang, Y., Ouyang, B., Xu, J., Chen, S., Rawat, R. S., and Fan, H. J. (2016). 3D Porous Hierarchical NickelâMolybdenum Nitrides Synthesized by RF Plasma as Highly Active and Stable Hydrogen-Evolution-Reaction Electrocatalysts. *Advanced Energy Materials*, 6(11):1600221.
- Zhao, Y. and Ouyang, G. (2019). Thickness-dependent photoelectric properties of MoS₂/Si heterostructure solar cells. *Sci Rep*, 9(1):17381. Number: 1 Publisher: Nature Publishing Group.
- Zhou, J., Liu, F., Lin, J., Huang, X., Xia, J., Zhang, B., Zeng, Q., Wang, H., Zhu, C., Niu, L., Wang, X., Fu, W., Yu, P., Chang, T.-R., Hsu, C.-H., Wu, D., Jeng, H.-T., Huang, Y., Lin, H., Shen, Z., Yang, C., Lu, L., Suenaga, K., Zhou, W., Pantelides, S. T., Liu, G., and Liu, Z. (2017). Large-Area and High-Quality 2D Transition Metal Telluride. *Advanced Materials*, 29(3):1603471.
- Zhu, J., Zhu, X., Liu, H., and Xing, J. (2021). *Thin Film Physics and Devices: Fundamental Mechanism, Materials and Applications for Thin Films*. WORLD SCIENTIFIC.
- Zhu, P. W., He, Z., Zhao, Y. N., Li, D. M., Liu, H. W., and Zou, G. T. (2002). Preparation of high-pressure phase boron nitride films by physical vapor deposition. *Journal of Vacuum Science & Technology A*, 20(3):622–624.
- Zhu, Z. Y., Cheng, Y. C., and Schwingenschlögl, U. (2011). Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors. *Phys. Rev. B*, 84(15):153402.

Appendix A

Appendix

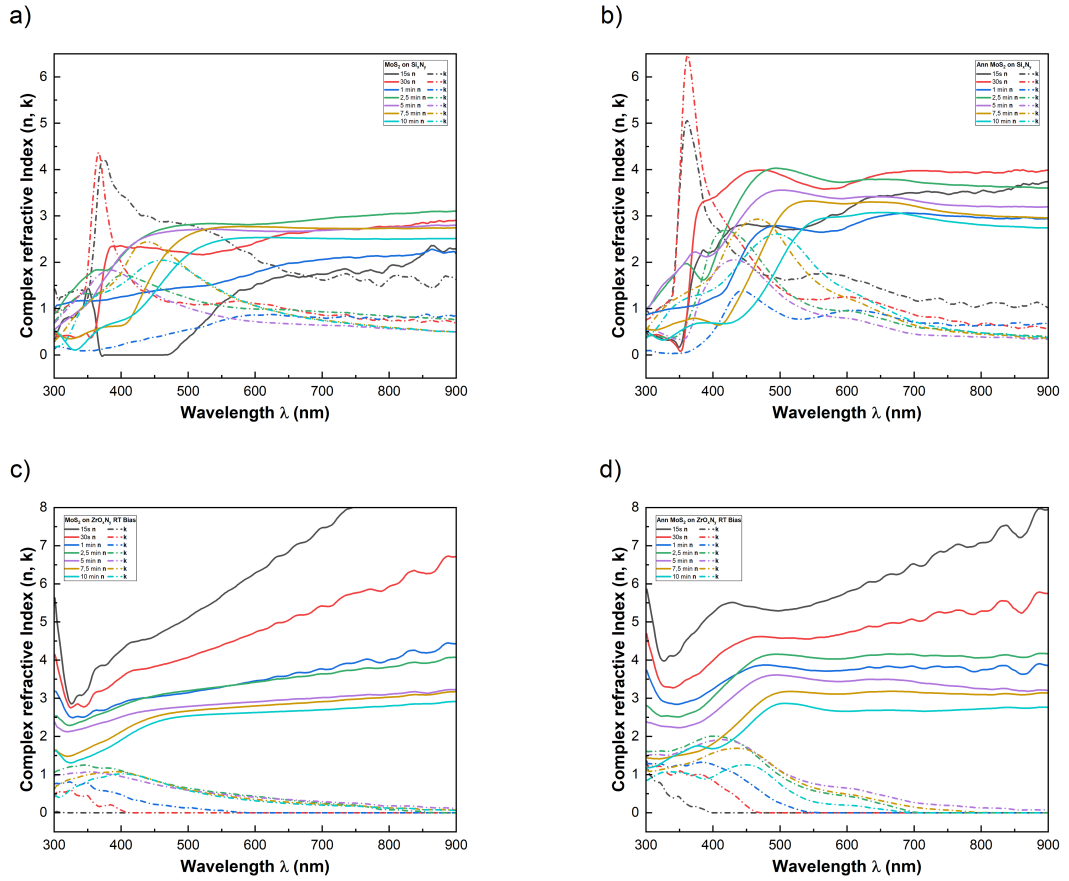


Figure A.1 – Complex Refractive Index (n, k) of **a)** MoS₂ on Si₃N₄ before annealing **b)** after annealing. MoS₂ on RT Bias ZrO_xN_y–Si₃N₄ **c)** before annealing and **d)** after annealing.

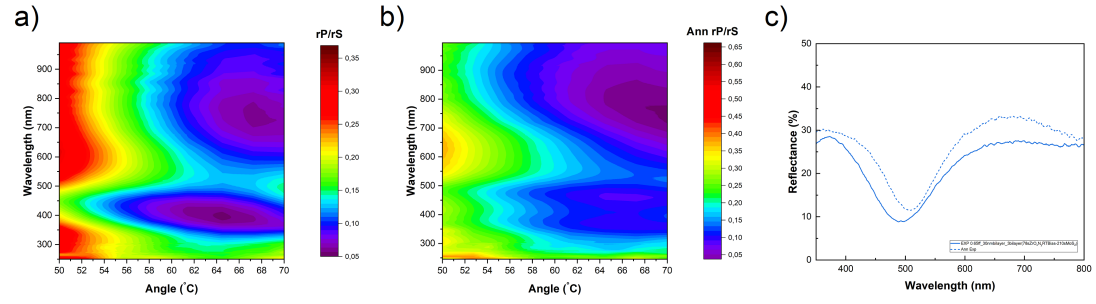


Figure A.2 – rP/rS measured experimentally as a function of wavelength and angle of incidence for a (65% ZrN) multilayer (ZrN–MoS₂) **a)** as-deposited, **b)** annealed at 485 °C and **c)** experimental (dotted lines) and simulated (bold lines) reflectance at normal incidence.



Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Title of work:

Multilayered Hyperbolic Metamaterial using 2D MoS₂
as Constituent

Metamaterial Hiperbólico Multicapa Utilizando MoS₂
Bidimensional como Constituyente

Thesis type and date:

Bachelor Thesis, December 12, 2023

Supervision:

Jose Luis Ocaña Pujol

Dr. Henning Galinski

Project Director

Eidgenössische Technische Hochschule Zürich (ETH Zürich)

(Chair: Prof. Dr. Ralph Spolenak)

Prof. Dr. German A. Perez

Project Co-Director

Universidad del Valle

Student:

Name: Ramon Camilo Dominguez Ordonez

E-mail: ramon.dominguez@correounivalle.edu.co

Statement regarding plagiarism:

By signing this statement, I affirm that I have read and signed the Declaration of Originality, independently produced this paper and adhered to the general practice of source citation in this subject-area.

Declaration of Originality:

http://www.ethz.ch/faculty/exams/plagiarism/confirmation_en.pdf

Zurich, 26. 2. 2024: